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NATURAL HYDROCARBON EMISSION RATE MEASUREMENTS FROM SELECTED FOREST SITES

by

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16. ABSTRACT

The report presents results from studies of biogenic hydrocarbon emissions conducted in Lancaster, Pennsylvania during 1979 and Seattle, Washington during 1980. The principal objective of the studies was to compare a branch enclosure method with a micrometeorological gradient technique for measuring biogenic hydrocarbon fluxes for forested areas. A second important objective for the Pennsylvania work was to develop a regional natural hydrocarbon emission inventory for use in the Northeast Regional Oxidant Study. Emission fluxes determined by the gradient profile procedure were in reasonably good agreement with those measured using the bag enclosure technique. Largest differences occurred at low emission levels and could partly be due to measurement uncertainty. Isoprene emissions from a deciduous forest in Lancaster, Pennsylvania correlated well with temperature. Alpha-pinene emission in a pine forest near Seattle, Washington correlated with ambient relative humidity. Total biogenic hydrocarbon emissions from the State of Pennsylvania was estimated to be 3400 tons/day during August.

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ABSTRACT

Studies of biogenic hydrocarbon emissions were conducted in Pennsylvania during 1979 and in Washington during 1980. The objectives of the Pennsylvania work were 1) to develop a regional natural hydrocarbon emission inventory for use in the Northeast Regional Oxidant Study; 2) to compare a branch enclosure method with a micrometeorological gradient profile technique for measuring biogenic hydrocarbon fluxes from a mixed deciduous forest; and 3) to compare the chemical composition of essential plant oils with the composition of biogenic gas emissions for selected species. In Washington, the branch enclosure technique and the gradient profile method were compared at a Douglas fir forest.

Four emissions categories based on similarities in composition and emission source were established in the Pennsylvania inventory. Isoprene emitting hardwoods, non-isoprene emitting hardwoods, monoterpene emitting softwoods and agricultural crops constituted the four groups. Volatile emissions from the isoprene emitting hardwoods were related to temperature in an exponential manner, with 78% of the total emission comprised of isoprene. A similar relationship between total hydrocarbon emission rate and temperature was found to exist for the non-isoprene emitting hardwoods. The estimated volatile emission from the non-isoprene group was 44% lower than the isoprene emitting species at 25°C. The monoterpene emitting softwoods release eight monoterpenes including: sabinene, camphene, α-pinene, β-pinene, myrcene, β-phellandrene, Δ^3-carene, and limonene.

A comparison between the composition of the volatile emissions and the needle and branch oils in conifers suggests that the source of the emission is the volatilization of these two oils.

Total biogenic hydrocarbon emissions from the state of Pennsylvania were calculated to be 3400 tons/day during August. Approximately 75% of these emissions were from forested lands and the remainder were from agricultural crops, primarily corn. The forest emissions were approximately evenly divided among the two categories of hardwoods and the softwood trees indicated above.

Isoprene emission fluxes determined by the gradient profile procedure in the deciduous forest were in reasonably good agreement with those measured using the enclosure technique. The isoprene flux from the gradient profile data was 10% higher than the enclosure flux at 30°C, but was approximately 3 times greater at 20°C. The differences at the low temperatures were possibly caused by the lack of profile data at the lower temperatures. The combined enclosure and gradient profile data were correlated with ambient temperature to the same degree as the correlation of each data set alone. In the Washington study, the alpha-pinene flux as measured by the gradient method ranged from 76 to 1,320 $\mu g/m^2$-hr while the range determined using the enclosure method was 9 to 700 $\mu g/m^2$-hr. The mean fluxes from the two methods were within the estimated limits of uncertainty. Alpha-pinene fluxes determined with the gradient profile method increased exponentially with increasing relative humidity. Emission fluxes calculated from the branch enclosure samples were not correlated with ambient relative humidity, but were strongly correlated with temperature when wet and dry branches were considered separately.

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SECTION 1

INTRODUCTION

The air chemistry of terpenes was first discussed by Went in 1960 (1). He suggested that aerosols produced by oxidation of volatile vegetative hydrocarbons could be the cause of "blue haze" associated with heavily vegetated areas like the Smoky Mountains.

The first evidence that natural hydrocarbons could produce ozone and aerosol particles was reported by Ripperton et al. in 1967 (2). Beginning in 1972, Washington State University (3,4) initiated a gas phase kinetic study to examine the photochemical reactivity of a number of monoterpenes that were known or were expected to be present in ambient forest air. The WSU study demonstrated that natural hydrocarbons were very reactive both in photochemical processes and ozonolysis reactions. Since studies have shown terpenes will produce O_3 photochemically (5), it is important that emission rates and ambient concentrations be established. This is especially true in light of reports of high ozone concentrations recorded in rural areas. It is for this reason that accurate measurements of biogenic hydrocarbon emission rates must be performed so that their contribution to the overall hydrocarbon burden of an area can be ascertained.

Considerable effort has been expended by a number of researchers in the characterization of biogenic hydrocarbon emissions. Two early measurements by Sanadze and Dolidze (6) and by Rasmussen (7) suggested that isoprene was a major constituent of the emissions. Subsequent work by Rasmussen (8) positively identified isoprene as being a biogenic emission product from several species.

Rasmussen (8,9) studied emissions from several species of deciduous and coniferous vegetation by placing a glass bell jar over a portion of the plant and measuring the buildup of terpenes as a function of radiation and temperature. Terpenes identified included alpha-pinene, beta-pinene, camphene, limonene, myrcene, and beta-phellandrene. Isoprene was found to be emitted by the hardwoods. Rasmussen observed that the rate of emission varied with the species maturity of the plant, integrity of the resin glands, and leaf temperature. Additionally, coniferous emissions were found to be independent of light while the emission of isoprene was light dependent with zero emission in the dark.

Tyson et al. (10) measured emissions from Salvia mellifera (California Black Sage) and estimated terpene emission levels of approximately 130 $\mu g/m^2$-hr. In a companion paper, Dement et al. (11) studied these emissions under varying light, humidity, and temperature conditions. They found that the volatilization rate of monoterpenes is dependent on the vapor pressures of the terpenes, humidity, and the amount of oil present on the surface of the leaf. These investigators also reported that the emission rate is not directly dependent on the photosynthetic activity or on the stomatal opening of the plant. This suggested that the mechanism was physical and that the terpenes were volatilized from the surface of the leaf rather than from the inside.

Tingey et al. (12) used a growth chamber to study the volatile emissions from live oak, and reported an average emission rate of approximately 30 μg/g leaf biomass/hr.

Arnts et al. (14), in a study similar to the gradient profile approach reported in this work, used a Bowen ratio technique to estimate the alpha-pinene flux from a loblolly pine plantation. An average flux of 3200 μg/m^2-hr was reported. They noted an increase in the emission flux with increasing temperature and water stress and decreased flux with increasing wind speed. They also observed substantially lower terpene concentrations in the winter months in samples collected 5 m above the canopy.

EPA and Duke University researchers (15) compared fluxes of alpha-pinene determined from the Bowen ratio technique to the results obtained using a branch enclosure method and observed good overall agreement. However, the enclosure procedure showed imprecision of ± one order of magnitude when examined versus temperature.

The most extensive study performed to date on the terpene emission rates from vegetation has been conducted by Zimmerman (16). His measurement technique involved enclosing a branch in a Teflon bag, evacuating air from the bag without damaging the branch, and refilling the bag with hydrocarbon-free air. After a few minutes, an air sample is extracted. He reported alpha-pinene emission rates from 0.07 to 4.8 μg/g-hr for five species of pine and isoprene emission rates of 0.1 to 44 μg/g-hr for seven species of oak in Florida.

Several attempts have been made to relate biogenic emission rates to measured ambient concentrations of terpenes above the vegetation. Holdren et al. (17) measured terpene concentrations in a canopy of mixed pine and fir in northern Idaho. They noted concentrations of alpha-pinene varied from .055 to 4.0 μg/m^3 one meter above the forest floor inside the canopy while total terpenes varied from 0.28 to 8.8 μg/m^3. Wind speed (ventilation) appeared to be the most important factor affecting terpene concentrations. Branch enclosure samples were also collected during the study and an average terpene emission flux of 3100 $\mu g/m^2$-hr was reported. The authors estimated an ambient terpene concentration equal to 8.8 $\mu g/m^3$ by assuming random eddy diffusion within the canopy. The authors concluded that normal atmospheric dilution processes could account for the low ambient terpene concentrations measured in rural atmospheres.

Zimmerman (18) reported an emission rate of isoprene from one live oak sample of 29 $\mu g/g$-hr. An ambient air sample collected 12 inches away from the branch contained 2.5 $\mu g/m^3$ isoprene. By using a box model, he concluded that the emission rate and the low concentration did not conflict.

Peterson and Tingey (19) reported a study which used measured emission rates and a simple box model to predict ambient concentrations of isoprene and monoterpenes in the southeastern United States during summer. They reported possible isoprene levels of 23 $\mu g/m^3$ and monoterpene levels of 70 $\mu g/m^3$. Although monoterpene emission rates are considerably smaller than the isoprene emission rate, observed monoterpene concentrations can be larger than the isoprene concentration because, unlike isoprene, monoterpenes continue to be emitted at night when atmospheric mixing is minimal.

Lonneman (20) reported a study of natural hydrocarbon emissions from a forested area of loblolly pine in North Carolina. Maximum concentrations of terpenes reported were 48 $\mu g/m^3$ alpha-pinene, 11 $\mu g/m^3$ beta-pinene, 1.8 $\mu g/m^3$ myrcene, and 2.7 $\mu g/m^3$ Δ^3-carene at ground level. Trace levels of terpenes were also observed in downwind samples.

A field project was conducted in the Smoky Mountains to study the relative importance of biogenic emissions in rural aerosol formation (21,22). Samples collected during an 8 day period showed biogenic hydrocarbons contributed from 6% to 28% of the total non-methane hydrocarbon (TNMHC) in the

Smoky Mountains. Isoprene concentrations measured ranged from only a trace to 12 $\mu g/m^3$ with an average of 4 $\mu g/m^3$. Four monoterpenes identified included alpha-pinene, beta-pinene, myrcene, and Δ^3-carene.

Dodge (23) used propylene, which is more efficient than alpha-pinene or isoprene in generating ozone, as a substitute for terpenes in a photochemical box model to predict the ozone formation potential of the terpenes. She used an emission rate of 6000 $\mu g/m^2$-hr propylene, 40 ppb O_3 background, and an NO_x flux of 720 $\mu g/m^2$-hr as starting conditions at 0700. The predicted maximum ozone concentration was 78 ppb while the hydrocarbon concentration reached a maximum of 14 $\mu g/m^3$ by mid morning. She concluded that biogenic emissions would not be the cause of episode levels of ozone observed in rural areas.

Recent measurements of natural emission rates suggest that natural hydrocarbons should constitute a significant portion of the hydrocarbons present in ambient air (9,16,18). For example, Zimmerman (24) reported that 68% of the total non-methane hydrocarbon emissions in the Tampa Bay region could be attributed to biogenic sources. However, at the same time that sizable quantities of biogenic emissions are being reported, ambient measurements of individual organic compounds show that natural compounds contribute negligible amounts to the total hydrocarbon burden. For example, natural organic emissions were determined to contribute 40-50% of the TNMHC emission rate in the Houston, Texas, region (18) while an analysis of ambient concentrations at a rural site outside of Houston indicated a contribution of only 2% (25).

In light of this discrepancy, the U.S. Environmental Protection Agency (EPA) has taken the position that natural hydrocarbons do not contribute significantly to the ozone problem and that reported biogenic emission rates are overestimated. For modeling purposes, EPA will determine biogenic emission rates by back-calculating natural emissions from ambient levels (26).

Even if natural emissions are negligible contributors to the ozone problem, the question of the discrepancy between anthropogenic and biogenic emission rates and their ambient concentrations remains a very important one. If the natural emission rates reported are indeed correct, then either ambient concentrations currently being reported are incorrect or reported anthropogenic hydrocarbon emission rates are in error, or the effects of atmosphere dilution, the different nature of biogenic and anthropogenic sources, and the different character of atmospheric chemical reactivities have not been properly recognized. Since mathematical models used to formulate oxidant control strategies employ emission rates as input information, the role of biogenic hydrocarbons should be correctly defined if the control strategies currently being formulated are to be realistic.

This report describes results from investigations of natural hydrocarbon emissions in Pennsylvania and Washington. The purpose of the work in Pennsylvania was to obtain emission rate data from the predominant vegetation in the northeastern U.S. and also to compare emission fluxes determined from a vegetation enclosure technique with those calculated from a micrometeorological gradient profile approach. The emission rate sampling program in Pennsylvania was designed to yield a biogenic hydrocarbon emission inventory for use in modeling studies in the Northeast Regional Oxidant Study (NEROS). In Washington, a second comparison of the enclosure and gradient profile methods was conducted in a Douglas Fir forest. An analysis of the systematic errors involved in each measurement method is also presented.

SECTION 2

CONCLUSIONS

This study has provided information regarding the character and magnitude of biogenic hydrocarbon emissions from vegetated regions in Pennsylvania and from a Douglas Fir forest in Washington. The two major objectives of the investigation were: 1) to obtain natural hydrocarbon emission rates from vegetation in the northeastern U.S. as a basis for modeling natural hydrocarbon fluxes in the Northeast Regional Oxidant Study (NEROS) and 2) to compare emission fluxes determined from a vegetation enclosure technique and a micrometeorological gradient profile method.

Northeastern Biogenic Hydrocarbon Emissions

Results from the Pennsylvania study indicate that volatile hydrocarbon emissions can be divided into four categories, based on similarities in composition and emission source. The first two categories are represented by hardwood trees that: (1) emit isoprene and (2) do not emit isoprene. The two remaining groups are the: (3) monoterpene emitting softwood trees and (4) agricultural crops.

Included in the group of hardwood trees that emit isoprene are oak, black locust, and sycamore. Isoprene, which is only emitted during daylight hours, accounts for 78% of the total volatile hydrocarbon emissions from this group. The emission rates are directly related to temperature in an exponential manner, with 90% of the variation in emission rates associated with temperature fluctuations. The regression relationship between temperature and emission rate predicts a total hydrocarbon emission rate of 6.1 μg/g-hr at 25°C.

The non-isoprene emitting hardwood trees include black gum, sassafras, tulip tree, red maple, dogwood, red hickory, black cherry, beech, silver maple, and birch. The hydrocarbon emissions from these species are also related to temperature in a exponential manner, with 91% of the variation in emission rates associated with temperature fluctuations. The regression relationship between temperature and emission rates predicts an emission rate of 3.4 μg/g-hr at 25°C. Major identified components of the volatile emissions are the monoterpenes: α-pinene, sabinene, β-pinene, myrcene, camphene, β-phellandrene, Δ^3-carene, and linalool.

The monoterpene emitting softwood species include: eastern white pine, Virginia pine, eastern hemlock, and pitch pine. The volatile emissions from this group consist of: α-pinene, sabinene, camphene, β-pinene, myrcene, α-phellandrene, limonene, and Δ^3-carene. These compounds comprise 50-95% of the volatile emissions. The composition of the volatile emissions is very similar to the composition of extracts obtained from the leaves and branches. This similarity suggests that the source of the volatile monoterpene emissions is the volatilization of the leaf and branch oils. Correlation between emission rate and temperature was not observed for this group and consequently the release of the monoterpenes must be controlled by some temperature independent process.

The agricultural crop category includes: tobacco, corn, clover, alfalfa and pasture. At present, this group is poorly defined and may require further divisions. The members emit compounds eluting near the monoterpenes and very small amounts of isoprene. There appears to be no relationship between emission rate and temperature.

The emission rates established in this study can be combined with vegetation surveys and biomass relationships to provide estimates of the magnitude of biogenic emissions. Total biogenic hydrocarbon emissions from the state of Pennsylvania were calculated to be 3400 tons/day during August. Approximately 74% of these emissions are from forested lands. The balance is estimated to result primarily from corn (25%) and from other agricultural crops and pasture. The forest emissions are approximately equally divided among isoprene-emitting hardwoods (887 tons/day), non-isoprene emitting hardwoods (711 tons/day) and conifer species (909 tons/day).

Comparison of Vegetation Enclosure and Micrometeorological Gradient Techniques

An important objective of this study was to compare biogenic emission measurements at a particular site using the branch enclosure method and a second independent approach based upon micrometeorological gradient profile procedures. Isoprene emission fluxes were determined with the two techniques at the oak forest in Pennsylvania during summer, 1979, and alpha-pinene emission fluxes were measured by both methods in a Douglas Fir forest in Washington during fall, 1980.

In Pennsylvania, isoprene fluxes measured by both techniques were observed to vary exponentially with temperature. The isoprene flux estimated from the enclosure data at 20°C ambient was 890 $\mu g/m^2$-hr and the flux calculated from the gradient profile data was 2510 $\mu g/m^2$-hr. At 30°C ambient, the difference between the two methods was approximately 10% (7300 $\mu g/m^2$-hr from the enclosure data and 8000 $\mu g/m^2$-hr from the gradient profile method). The differences at 30°C are within the estimated experimental uncertainty of the two methods of measurement, but the results at the lower temperature are not within the error limits. However, very few gradient profile experiments were conducted at low temperatures. Furthermore, the combined data from the enclosure and gradient profile measurements are correlated with ambient temperature to the same degree as either data set alone. As a result, the data obtained in Pennsylvania indicate that the two independent methods for measuring isoprene flux yield results which are in reasonable agreement.

The fluxes calculated from the gradient profiles were also observed to increase exponentially with increasing heat flux, with increasing intensity of turbulence as measured by $\sigma_\theta u_z$ and also with the parameter $T_z u_z$. These relationships did not exist with the fluxes measured by the enclosure technique. Isoprene concentrations measured above the canopy increased exponentially with increasing ambient temperature.

In Washington, alpha-pinene flux measured via the gradient profile technique and ambient concentrations measured above the canopy both increased exponentially with increasing relative humidity over a range of relative humidity greater than approximately 60%. Alpha-pinene fluxes were only weakly correlated with ambient temperature. The mean flux of alpha-pinene measured by 7 gradient profile experiments was 440 $\mu g/m^2$-hr (median = 230 $\mu g/m^2$-hr) with a range of 76 to 1320 $\mu g/m^2$-hr.

The mean alpha-pinene flux estimated from 13 enclosure samples was 150 $\mu g/m^2$-hr (median = 46 $\mu g/m^2$-hr) with a range of 9 to 700 $\mu g/m^2$-hr. No relation between ambient relative humidity and alpha-pinene flux was observed with the enclosure data. However, when the samples were grouped according to wet and dry branches, a distinct exponential relationship with increasing ambient temperature was evident.

No single environmental parameter was correlated with the fluxes determined by both methods. As a result it was not possible to compare directly fluxes predicted for a common reference point as was done for isoprene as a function of temperature. The mean flux of alpha-pinene for the gradient profile experiments and the mean flux predicted by the enclosure samples were within experimental uncertainties estimated for the two methods. The wide range of fluxes observed is not a result of random experimental errors. Rather, changes in environmental conditions such as temperature and humidity were observed to affect the emission rates dramatically. In view of the strong dependence of flux upon humidity, the low fluxes determined with the enclosure method suggest that humidity inside the bag was generally lower than ambient.

The error limits estimated for the two techniques were based upon standard error analysis procedures. Data from typical experiments were combined with estimated or measured uncertainties in the independent variables to calculate the overall error and degree of reproducibility in each flux method. In Pennsylvania, the error in the gradient profile method was estimated to equal ± 35% and in Washington, the error was approximately ± 55%. The major sources of error were uncertainties in the zero plane displacement height and the hydrocarbon concentration gradient. The gradient profile method is estimated to be reproducible to within less than ± 17% for tests conducted at a specific site. The overall error estimated for a typical enclosure sample was ± 40% and the technique was estimated to be reproducible to within ± 20% for samples collected in a particular forest.

Based upon a Gaussian volume source dispersion model, the concentrations of isoprene and alpha-pinene measured at the canopy top were found to be consistent within a factor of two with the respective fluxes obtained with gradient profile measurements.

In both studies, the fluxes obtained with the enclosure technique were found to be generally less than the fluxes obtained with the gradient profile approach. This difference in the emission fluxes could possibly be due to the following factors:

(1) enclosing a branch inside a bag alters the emission mechanism to such an extent that the flux obtained would not be comparable with any environmental parameter either inside or outside the bag. This has been shown to be untrue both in this study and others. The enclosure data exhibited a strong correlation with temperature in both Pennsylvania and Washington. Other researchers have also reported this relationship with temperature (27).

(2) Extrapolation of the biomass emission fluxes using the biomass (g/m^2) of the forest could lead to an underestimation of the flux if any isoprene or alpha-pinene-emitting biomass were not included in the biomass conversion factor. In the Pennsylvania study, biomass factors from available biomass relationships varied by ± 30% relative to the algorithm used in the calculation. This kind of error is potentially large in the development of regional emission inventories.

(3) Emission rates measured at ground level are not representative of the flux observed from the top of the canopy. Samples were most often collected in semi-open to open areas most resembling the conditions near the canopy top. Samples were collected from both old and new growth with no significant differences being observed. Therefore, the samples collected were considered representative of the forest as a whole.

(4) Both study sites were acceptable for consideration as an infinite, uniform area source subject to treatment via surface layer theory. In each case, care was taken to accept test results only if the upwind fetch was large

relative to the sampling heights. Therefore it is reasonable to assume that all measurements were performed in the equilibrated boundary layer.

(5) The flux obtained by the enclosure method may be representative only of the conditions inside the bag, and attempts to correct bag conditions to ambient conditions may not be adequate. In both studies, it was evident that the conditions inside the bag were different from ambient; at times this difference was extreme. In particular, the Washington data suggest that the humidity inside the bag was generally lower than ambient. It is strongly suggested that a more thorough measurement of the conditions both inside and outside the bag be performed routinely in all future studies when using the enclosure technique.

SECTION 3

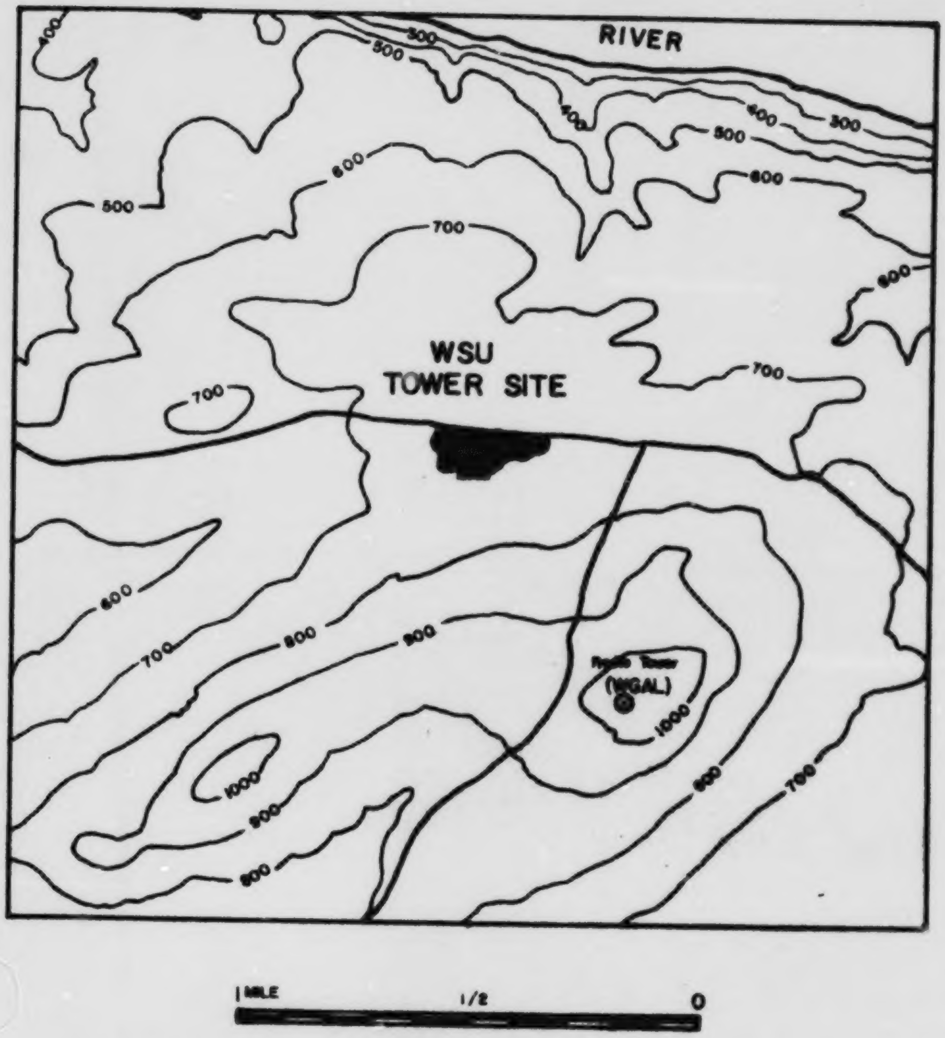
EXPERIMENTAL METHODS

The sampling program was completed in two parts. The first phase concentrated on measuring hydrocarbon emissions in a predominantly oak forest and from other vegetated sites near York, Pennsylvania during August, 1979. The second phase was designed to measure monoterpene emissions in a predominantly Douglas Fir forest near Seattle, Washington, in October and November, 1980. Both studies were performed in essentially the same fashion with small differences being dictated by the site requirements and equipment availability.

Site Description

Pennsylvania. The Pennsylvania forest was located approximately 10 km northeast of York, Pennsylvania at 40°02' latitude, 76°37' W longitude in Hellam Township, York County, Pennsylvania. The location is on a level area 235 m above sea level. A topographic map of the area is shown in Figure 1. The study area was characterized by flat or gently rolling terrain in the east-west direction and by uniformly sloping ground which varied between 100 and 300 meters in the north-south direction. A uniform fetch in excess of 1.6 km extended to the southeast and southwest of the tower and 1.2 km to the south.

A vegetation inventory conducted by Parks during August, 1979, (Appendix 1) indicated that the woodland studied was representative of a second growth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Radio Tower
(WGAL)
1000
1000
900
800
900
700
1 MILE
1/2
0

Figure 1. Pennsylvania study area topography. Contour lines in feet above sea level.

oak-chestnut forest. Four species of oak, Quercus velutina (Black Oak), Quercus prinus (Chestnut Oak), Quercus coccinea (Scarlet Oak), and Quercus alba (White Oak), comprise 77.5% of the individuals present with their size (biomass) in proportion to their numbers. Other species present in the overstory included Liriodendron (Tulip Poplar), Robinia (Locust), Prunus serotina (Black Cherry), and Betula lenta (Sweet Birch). The understory was comprised of Nyssa (Tupelo), Sassafras, Betula lenta (Sweet Birch), Cornus (Dogwood), Acer rubrum (Red Maple), and Toxicodendron (Poison Ivy). The average canopy height was estimated to be 20 m. A 34 m tower erected at the north edge of a clearing was utilized for the collection of the gradient samples. The branch enclosure samples were collected in the immediate vicinity of the tower. Meteorology during the study period was typical of Eastern U.S. summertime conditions; the days were generally hot and humid with occasional afternoon thunderstorms. Winds were usually from the south and west.

Washington. The Washington study area was located approximately 30 km southeast of Seattle, Washington in the A. E. Thompson Research Forest (University of Washington). The forest was located approximately 215 m above sea level at 47°20' N latitude, 122°30' W longitude. A 39 m tower erected by the University of Washington School of Forestry was utilized for the collection of the gradient samples. The area surrounding the tower was level in the east-west directions; a small hill rising 20 m was located approximately 200 m due north of the tower and a ridge rising 30 m ran in an east-west direction 200 m due south. The uniform fetch in the east-west direction was greater than 1.6 km. A topographic map of the area is shown in Figure 2.

The forest consisted almost entirely of Pseudotsuga menziesii (Douglas Fir)

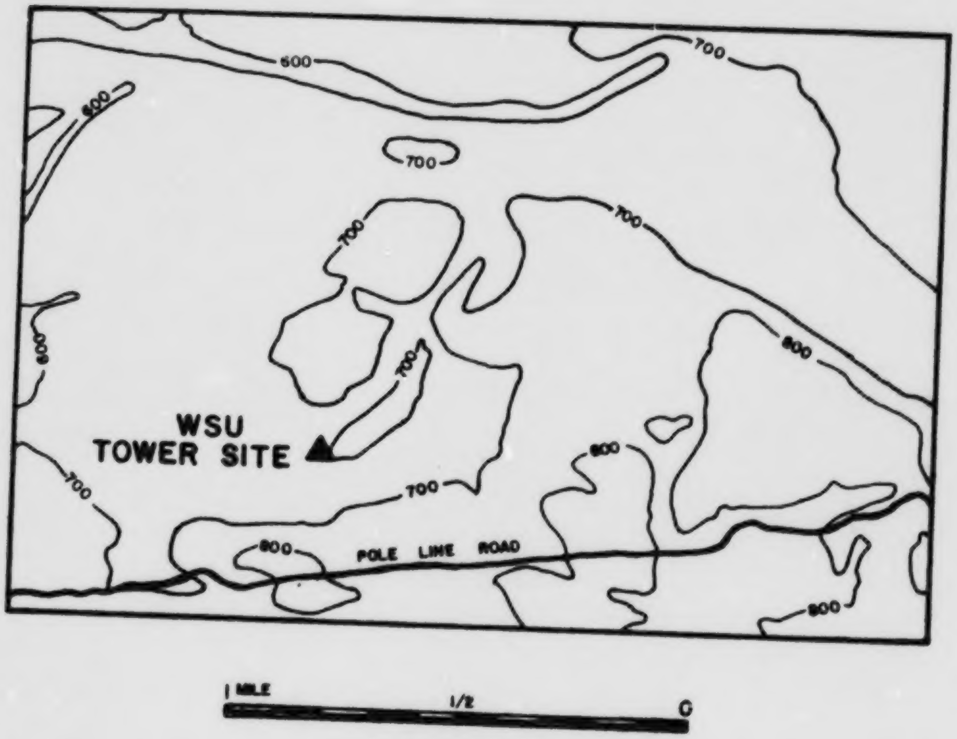

600
700
700
700
700
700
800
600
WSU
TOWER SITE
800
700
700
800
POLE LINE ROAD
800
1 MILE
1/2
0

Figure 2. Washington study area topography. Contour lines in feet above sea level.

with associated secondary species Alnus rubrum (Red Alder), Tsuga heterophylla (Western Hemlock), and Thuja plicata (Western Red Cedar) present in small amounts (28). The age of the stand was found to be 52 years (29) and the average canopy height was approximately 31 m. Meteorological conditions during the study period were generally typical of the Pacific Northwest coastal climate: cool, low clouds, and wet most of the time. High wind speed, low humidity, and clear sky conditions were only encountered during two tests. The prevailing winds were from the west.

The Gradient Profile Method

Mass transport by vertical turbulent diffusion proceeds with the flux through a horizontal plane given by

$$F = \overline{w'C'} = K_z \frac{\partial C}{\partial z} \tag{1}$$

where $\overline{w'C'}$ is the time-averaged product of vertical velocity and concentration fluctuations. That the flux is also proportional to the concentration gradient, analogous to molecular diffusion, is an assumption invoked to solve the closure problem of turbulence. The proportionality constant K_z is the eddy diffusivity, which for a uniform, infinite surface is a function of the stability of the atmosphere, the roughness of the underlying surface, and the height above the surface. In order to determine the flux of a gas to or from the surface, the concentration gradient must be measured and a value of K_z must be calculated from measured properties of the turbulent atmosphere.

As a first step it is generally assumed that K_z (mass) is equal to the eddy heat and momentum diffusivities K_H and K_m, and the corresponding heat and momentum fluxes are written

$$H = -\rho C_p K_H \frac{\partial \theta}{\partial z} \tag{2}$$

$$\tau = \rho K_m \frac{\partial u}{\partial z} \qquad (3)$$

where ρ is the density of air, C_p is the specific heat of air (0.240 cal/g-°K), $\partial\theta/\partial z$ is the local vertical potential temperature gradient ($\approx \partial T/\partial z - \Gamma$); $\partial T/\partial z$ is the local vertical temperature gradient and Γ is the dry adiabatic lapse rate = .0098 °K/m) and $\partial u/\partial z$ is the local vertical wind speed gradient.

The terms in eq. (2) and (3) can be rearranged to yield non-dimensional vertical profiles:

$$\phi_H = - \frac{\rho\ C_p\ k u_* z}{H} \partial\theta/\partial z \qquad (4)$$

$$\phi_m = \frac{kz}{u_*} \partial u/\partial z \qquad (5)$$

where u_* is called the friction velocity (m/s) which is a measure of frictional forces at the surface and k is the von Karmon constant which is usually assumed to equal 0.4. At this point, there are still four unknowns (ϕ_H, ϕ_m, H, u_*) in the two equations. However, very careful and complete measurements from a number of investigators have provided empirical expressions for ϕ_H and ϕ_m as functions of a non-dimensional height (z/L) where L is an atmospheric stability parameter called the Monin-Obukhov length (30). Although there is some debate over the proper form of the empirical expressions for the non-dimensional profiles, the following have been widely used (30):

Unstable

$$\phi_H = [1 - 16\ (z/L)]^{-\frac{1}{2}} \qquad L<0 \qquad (6)$$

$$\phi_m = [1 - 16\ (z/L)]^{-\frac{1}{4}} \qquad (7)$$

Neutral

$$\phi_H = \phi_m = 1 \qquad L \to \infty \qquad (8)$$

Stable

$$\phi_H = \phi_m = 1 + 4.7\ (z/L) \qquad L>0 \qquad (9)$$

The Monin-Obukhov length is a characteristic length developed from dimensional arguments to characterize the relative importance of mechanical and buoyancy driven turbulence in a particular flow situation. It is defined as

$$L = -\frac{\rho C_p u_\star^3 \theta}{kg H} \qquad (10)$$

where θ is a reference potential temperature and g is the acceleration due to gravity. During unstable conditions, L is negative, and during stable conditions, L is positive. In neutral situations, the heat flux is zero and L goes to infinity.

With the non-dimensional profiles available from the empirical expressions, eq. (4) and (5) can be rearranged and integrated to obtain expressions for u(z) and $\theta(z)$ as functions of (z/L) (31):

Unstable

$$u_z = \frac{u_\star}{k}\left(\ln (z/z_o) + \ln \left[\frac{(\beta_o^2 + 1)\ (\beta_o + 1)^2}{(\beta^2 + 1)\ (\beta + 1)^2}\right] + 2 \tan^{-1}\beta - \tan^{-1}\beta_o \right) \qquad (11)$$

where $\beta = [1 - 16\ (z/L)]^{\frac{1}{4}}$ and $\beta_o = [1 - 16\ (z_o/L)]^{\frac{1}{4}}$

$$(\theta_z - \theta_o) = \theta_\star \left(\ln (z/z_o) + 2 \ln \left[\frac{\lambda_o + 1}{\lambda + 1}\right]\right) \qquad (12)$$

where $\lambda = [1 - 16\ (z/L)]^{\frac{1}{2}}$ and $\lambda_o = [1 - 16\ (z/L)]^{\frac{1}{2}}$

Neutral

$$u_z = \frac{u_\star}{k} \ln (z/z_o) \qquad (13)$$

$$\theta_z - \theta_o = 0 \qquad (14)$$

Stable

$$u_z = \frac{u_\star}{k}\left(\ln\ (z/z_0) + 4.7\ (z/L)\right) \tag{15}$$

$$(\theta_z - \theta_0) = \theta_\star\left(\ln\ (z/z_0) + 4.7\ (z/L)\right) \tag{16}$$

where z_0 is the surface roughness length, θ_0 is the temperature at z_0, and $\theta_\star$ is a scaling temperature (analogous to $u_\star$) defined as

$$\theta_\star = \frac{-\ H}{\rho C_p k u_\star} \tag{17}$$

At this point, available wind speed data from two or more heights from neutral situations can be used to determine the surface roughness length z_0:

$$z_0 = \exp\left[\frac{u_2 \ln z_1 - u_1 \ln z_2}{u_2 - u_1}\right] \tag{18}$$

With z_0 known, the appropriate expressions for u_z and θ_z can be iteratively solved simultaneously to obtain best-fit profiles where $u_\star$ and $\theta_\star$ are the best-fit coefficients. The best-fit procedure used in this work is similar to a method outlined by Nieustad (32) in which the wind and temperature profiles are combined in a single function

$$G(u_\star,\theta_\star) = \sum_{i=1}^{N_u}\Big[(u_m(i) - u_z(i))/u_e\Big]^2 + \sum_{i=1}^{N_\theta}\Big[\Big((\theta_m(i) - \theta_z(i)) - (\theta_m(1) - \theta_z(1))\Big)/\theta_e\Big]^2 \tag{19}$$

where N_u and N_θ are the number of wind and temperature observation levels, the subscript m refers to measured values, and u_e and θ_e are estimated errors in the measured parameters which act to weight the wind and temperature measurements equally. The form of G eliminates dependence upon θ_0 which is an unknown parameter. A non-linear numerical process, called the Marquardt technique, is used to find the values of $u_\star$ and $\theta_\star$ which minimize $G(u_\star,\ \theta_\star)$.

Following the best-fit process, the heat flux can be calculated directly from the definition of θ_* and the Monin-Obukhov length can also be determined. Substitution of (4) and (5) into (2) and (3), respectively, then yields expressions for the eddy diffusivities

$$K_H = \frac{ku_* z}{\phi_H} \qquad K_m = \frac{ku_* z}{\phi_m} \tag{20}$$

where all terms are known. In our application of this procedure, we assumed that K_z (mass) equaled K_H for all stability conditions.

There remains one complicating factor associated with the use of these equations for a forested area. For tall vegetation, the vertical profiles of wind speed and temperature are displaced upward a height dependent mainly upon the height of the vegetation. This zero plane displacement height d represents an imaginary surface where the property fluxes become zero and where at $d + z_0$, the wind speed equals zero. To a rough approximation, d is in the range .6h to .7h where h is the height of the vegetation. To incorporate d into the equations, all heights are rewritten as z-d where z is the height above the ground; for example, $K_H = ku_*(z-d)/\phi_H$.

In our application of the gradient profile method, we followed the suggestion of Hicks and Wesley (33) and assumed that d = 0.7h. This yields d = 14.0 m for the Pennsylvania site and d = 21.4 m for the Washington forest. The displacement height can be determined from wind profiles measured during neutral conditions. In a linear regression analysis of wind speed versus ln(z-d), the correct value of d yields the maximum linear correlation coefficient. In Pennsylvania, there were few instances of neutral stability. In Washington, the linearization procedure was found to be extremely insensitive to rather large changes in d. For example, in one case changing d from 29 m to 21 m caused the correlation coefficient to change only from 0.994 to 0.985. As a result, it was not possible to calculate a consistent value of d from the neutral wind speed profiles. For this reason, we assumed d = 0.7h as indicated above and we calculated z_0 from eq (18) for all of the available neutral situations. In Pennsylvania, the mean and standard deviation of the calculated surface roughness equaled 0.94 ±0.16 m and in Washington, the mean and standard deviation of the surface roughness was 3.54 ±1.65 m. In an earlier study at the Washington site, Gay and Stewart (34) reported a displacement height of 23 m and a surface roughness of 3.92 m.

The Branch Enclosure Method

The branch enclosure method described by Zimmerman (27) combines the advantages of a static enclosure system with a dynamic flow system. Figure 3 illustrates the equipment setup involved in collecting an enclosure sample. The method involves enclosing a portion of a branch of interest in a Tedlar bag, evacuating most of the ambient air, and collecting a "background" sample from the removed air. The bag is then reinflated with a known volume of hydrocarbon-free air. After the bag has been filled with the zero air, another sample is collected while the zero air continues to flow into the bag at the same rate the sample is being withdrawn. The difference between the hydrocarbon content of the bag at the two sample periods divided by the time interval (usually ~6 min) between samples and the dry weight of enclosed leaves (needles) gives the emission rate. The branch is enclosed for a total time of approximately 15 minutes. Table 1 shows the procedure for calculating emission fluxes from the branch enclosure method.

Inherent in the enclosure procedure for predicting isoprene and alpha-

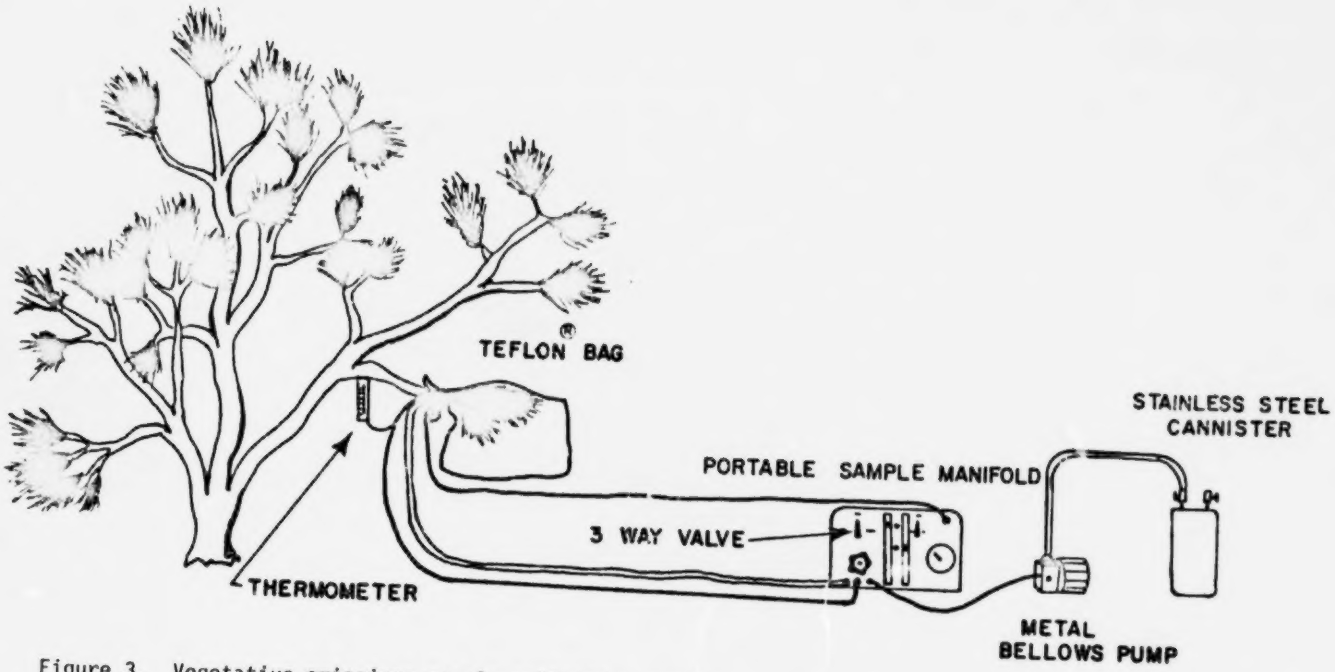

TEFLON® BAG
THERMOMETER
3 WAY VALVE
PORTABLE SAMPLE MANIFOLD
METAL BELLOWS PUMP
STAINLESS STEEL CANNISTER

Figure 3. Vegetative emissions sample collection system.

TABLE 1. CALCULATION OF EMISSION FLUX FOR ENCLOSURE SAMPLES

$$EF = \frac{S(V_1 + V_2) - (BV_2)}{TM} \times F$$

EF = isoprene or alpha-pinene emission flux (μg/m^2-hr).

S = isoprene or alpha-pinene concentration in the emission sample (μg/m^3).

B = isoprene or alpha-pinene concentration in the background sample (μg/m^3).

V_1 = volume of zero air metered into the enclosure (m^3).

V_2 = dead volume of the bag when collapsed around the branch (m^3).

T = total sample time. This is the time interval between the background sample and the emission sample (hr).

M = dry weight of the leaves or needles (g).

F = biomass conversion factor for the study site (g/m^2).

pinene fluxes are the following assumptions: (1) the emission rate measured for the enclosure branch is identical to that which would be observed for an unenclosed branch; and (2) the emission rate from a single branch is representative of the emission rate from all branches of all trees of the same species in the forest. It is also assumed that the hydrocarbon emission rate for a given set of conditions does not vary from species to species.

An uncertainty analysis was performed on the enclosure method of determining biogenic emission rates in order to estimate the precision and accuracy of the calculated flux. The analysis was based upon the accuracies of the individual measurements which were used to calculate the flux. A complete description is given in Appendix 2. The error limits in the calculated flux were estimated to be ± 40%, and the reproducibility of the enclosure method was calculated to equal ± 20%. Any variation in the measured flux over and above 20% from test to test was expected to reflect physiological or environmental differences in the samples and not random experimental errors.

Determination of Forest Biomass

If the individual branch emission rates measured by the enclosure method are to be used to estimate regional biogenic emission fluxes, a biomass factor (g/m^2) must be obtained to convert the emission rates ($\mu g/g$ leaf biomass/hr) to emission fluxes ($\mu g/m^2$-hr). Several methods exist for performing this conversion.

The procedure followed in Pennsylvania utilized a regression equation relating biomass to the diameter of a tree at breast height (DBH) (35). This method is based upon the principle that tree dimensions will maintain their functional balance as they enlarge. A vegetation inventory conducted at the site by Parks (see Appendix 1) indicated that isoprene-emitting hardwoods accounted for approximately 65% of the total biomass of the forest. From this information, the isoprene-emitting biomass of the study site was determined to be 379 g/m^2 and the total biomass at the site was 583 g/m^2.

The procedure utilized in Washington employed a relationship between biomass and the age of a Douglas Fir determined from the study site (36). Assuming that terpene-emitting Douglas Fir accounted for 100% of the total biomass of the forest, the biomass of the study area was determined to be 830 g/m^2.

Enclosure Sample Analysis

Our field laboratory was located at Franklin and Marshall College in Lancaster, PA. Analytical instrumentation was set up in laboratory space provided by the Biology department. Natural hydrocarbon emission samples were collected primarily at the forest site; a few samples were collected in Lancaster in order to obtain a larger range of species.

Stainless steel canisters were used to collect all hydrocarbon samples. These canisters have had their inner surfaces deactivated by the "Summa" process. The cans were filled with air using a metal bellows pump and sealed by closing two bellows valves. By pressurizing these containers to 10 psig, about 5 liters of air was obtained for sampling purposes.

Gas chromatographic analyses were performed with a Perkin Elmer 3920 GC for species in the C_2-C_5 molecular weight range and with Hewlett Packard 5700 and PE Sigma 3 GC's for hydrocarbons between C_5 and C_{10}. A PE Sigma 10 data system served as the integration and reporting device for quantitation of individual hydrocarbons from all chromatographs. Additional details are provided in a subsequent section.

Hydrocarbon quantitation was achieved by determining the peak area corresponding to a given volume of 0.204 ppm neohexane (2,2-dimethylbutane). It was assumed that the neohexane nanogram per area count response was valid for all hydrocarbons on a per carbon basis. The .204 ppm neohexane standard was obtained from Scott Environmental Laboratories. The .204 ppm concentration was confirmed by comparing it to a series of hexane standards prepared in our laboratory. A measured volume of hexane was injected into an evacuated cylinder which in turn was pressurized with a known volume of hydrocarbon free air. This provided hexane concentrations in the ppm range. Sub-ppm levels were obtained by transferring an aliquot from the cylinder to a second canister which was then pressurized and a new concentration calculated.

The .204 ppm neohexane standard was run on each chromatograph approximately every other day during the study period. If the area counts for a 100 ml injection of this external standard varied more than 10% from the previous run, ambient sample analysis was discontinued until the reason for the variance was determined. The standard deviation for 20-25 neohexane runs on each GC system during the study period typically fell in the range of 5 to 7%.

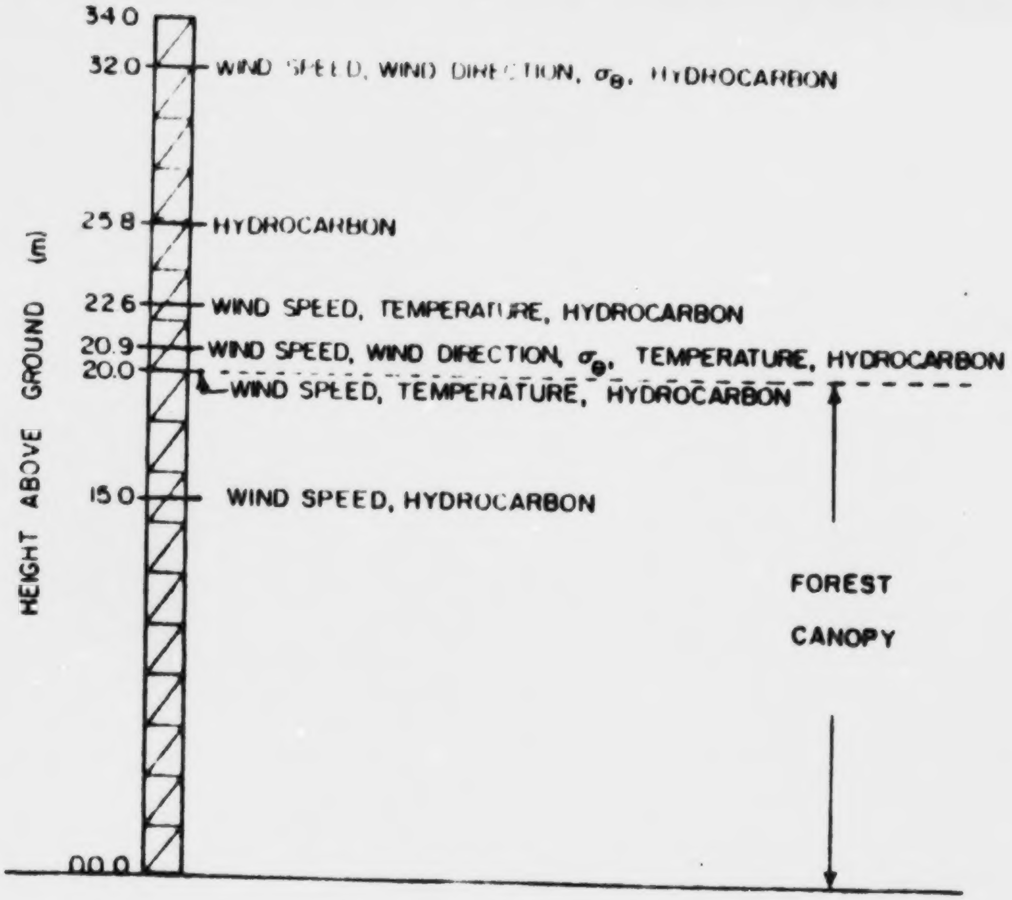
The concentration of each individual hydrocarbon (in micrograms/m^3) was determined by multiplying the area counts as reported by the GC data system by a factor which incorporated the standard area counts/μg and the necessary volume conversions. Concentrations in ppbC units were obtained by multiplying μg/m^3 by 1.5.

Meteorological Measurements

Pennsylvania. Meteorological sensors were positioned at six levels on the tower, as shown in Figure 4. All sensors were manufactured by Climet Instrument Company. Wind speed was measured by cup anemometers with a factory-specified accuracy of ± 2%. Temperature measurements were obtained by platinum thermistors accurate to ± 0.15°C housed in aspirated radiation shields. Wind direction sensors were potentiometric 540° output with σ_θ determined from electronic treatment of the wind direction signal. Meteorological data were collected continuously and recorded as 30 minute averages using a Monitor Labs 9300 data logger located in a trailer at the base of the tower.

Washington. The same meteorological sensors as described above were also utilized in Washington. Sensor locations are shown in Figure 5. Meteorological data were collected continuously and recorded on 4-track tape by a DL 620 Metro data logger. The tapes were returned to Pullman, Washington where they were copied to 9-track tape, reduced, and tabulated as 30 minute averages.

Sensor Calibration. In order to utilize the gradient technique effectively and accurately, temperature and wind speed sensors must be capable of measuring very small changes with height. An intercomparison was performed to improve the factory-specified interchangeability of the temperature and wind speed sensors. In Pennsylvania, both wind speed and temperature sensors were compared in the field by operating all sensors for several hours at the same location approximately 1 m above the ground. For the Washington work, temperature thermistors were bound together and the tips immersed with a mercury thermometer



34.0
32.0
WIND SPEED, WIND DIRECTION, σ_θ, HYDROCARBON
25.8
HYDROCARBON
22.6
WIND SPEED, TEMPERATURE, HYDROCARBON
20.9
WIND SPEED, WIND DIRECTION, σ_θ, TEMPERATURE, HYDROCARBON
20.0
WIND SPEED, TEMPERATURE, HYDROCARBON
15.0
WIND SPEED, HYDROCARBON
00.0
HEIGHT ABOVE GROUND (m)
FOREST
CANOPY

Figure 4. Pennsylvania tower sensor location.

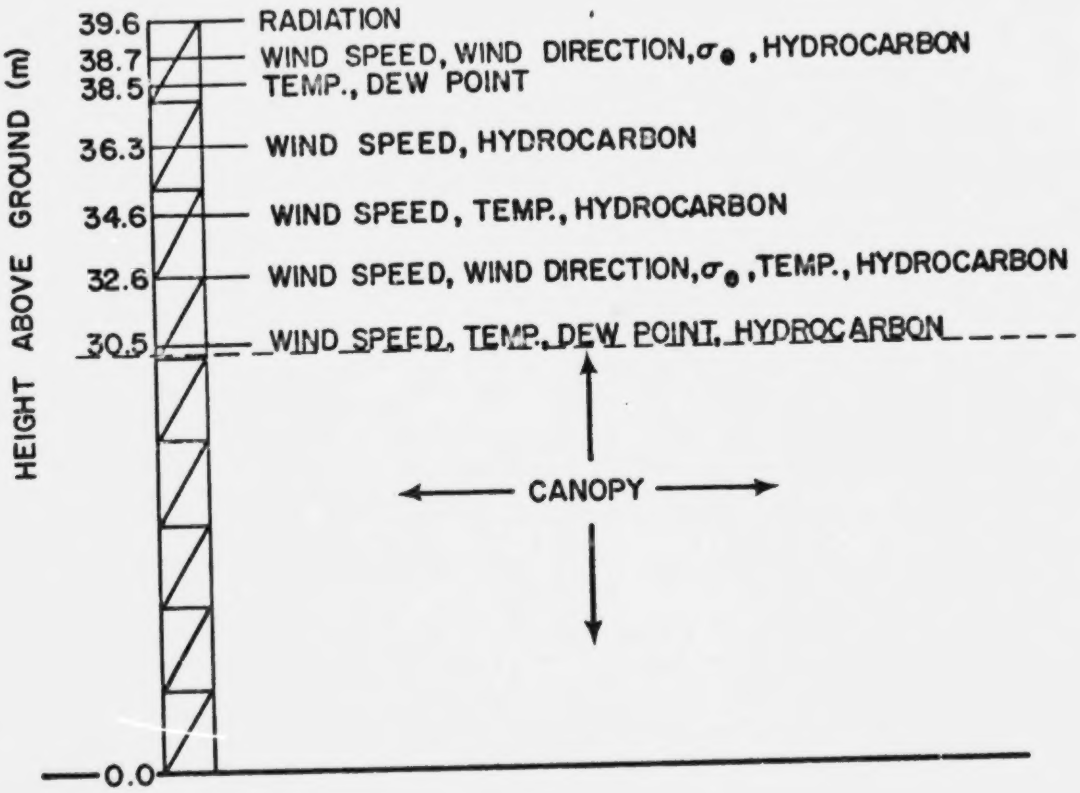

HEIGHT ABOVE GROUND (m)
39.6
38.7
38.5
36.3
34.6
32.6
30.5
0.0
RADIATION
WIND SPEED, WIND DIRECTION, σ_θ, HYDROCARBON
TEMP., DEW POINT
WIND SPEED, HYDROCARBON
WIND SPEED, TEMP., HYDROCARBON
WIND SPEED, WIND DIRECTION, σ_θ, TEMP., HYDROCARBON
WIND SPEED, TEMP., DEW POINT, HYDROCARBON
CANOPY

Figure 5. Washington tower sensor location.

(0.1°C gradations) in ice water which was kept well mixed with a magnetic stirrer. The mercury thermometer was read periodically as the temperature slowly rose to 17°C. Data was collected continuously with the Metro data logger and tabulated as 1-minute averages. Each thermistor was referenced to the mercury thermometer and a regression equation for each sensor was utilized to convert field readings to the common reference. From an examination of the residuals around the regression line, the variation between sensors was determined to be ± 0.01°C.

Wind speed sensors were calibrated in a wind tunnel at WSU. Each sensor was placed in the tunnel and outputs, scanned twice a second, were recorded for ten minutes. This was performed at three speeds for each anemometer. One sensor recently calibrated at the factory was used as the reference and again regression lines were used as correction factors. The variation between wind speed sensors was determined to be ± 0.07 m/s from an examination of the residuals around each regression line.

Hydrocarbon Gradient Sampling and Analysis

Pennsylvania. Thirty minute average hydrocarbon samples were collected at six locations along the tower as shown in Figure 4. Samples were collected in 6 ℓ Tedlar bags equipped with Teflon sampling pumps and hoisted aloft in styrofoam boxes. Tests were performed only during conditions with wind blowing from across the forest. The hydrocarbon samples, sheltered from sunlight, were transported 20 miles to Lancaster, Pennsylvania for analysis. Tests of sample stability indicated that isoprene concentrations changed by less than 5% during overnight storage in the bags. Most samples were analyzed on the same day as collected and all samples were analyzed within 24 hours of collection using a

Perkin Elmer 3920 gas chromatograph equipped with a 20' X 1/6" stainless steel Durapak n-Octane/Porasil C column (Waters Associates, Framingham, Massachusetts), subambient accessory, and a flame ionization detector. In addition, a freezeout loop was employed to enrich the sample before injecting it onto the head of the column. The loop was filled with 60/80 mesh glass beads and was immersed in liquid oxygen. When the sample concentration step was complete, the loop was immersed in boiling water to flush the organics trapped in the loop onto the head of the column. Good separation of isoprene was achieved with a temperature program of -65°C to 80°C at 16°C/min with an initial delay time of four minutes. Neohexane was used as the quantitative standard for all chromatographic analyses. A nanogram per area count response was determined and that same value was then assigned to all of the hydrocarbons. The neohexane standard was run periodically to insure stability of response. The detection limit was determined to be 0.02 $\mu g/m^3$ for a 3 ℓ sample. The uncertainty in the absolute accuracy obtained with the chromatographic technique is assumed to be less than ± 10%.

Washington. Thirty minute average hydrocarbon samples were collected at five locations on the tower as shown in Figure 5. Samples were collected in stainless steel tubes packed with 0.5 g Tenax-GC, a solid adsorbent discussed in greater detail below. Each tube was connected by polyethylene tubing to a pump on the ground. The entire sampling manifold was hoisted aloft using a pulley system on the side of the tower. Glass capillaries downstream of the tubes restricted flow to approximately 100 cm^3/min; the exact flows were measured during each test with a wet test meter. In this manner, approximately 3 ℓ samples were collected in each tube. Samples were then capped and air freighted to Pullman, Washington for analysis. All samples were analyzed within approximately 36 hours of collection.

Tenax. Tenax-GC (Applied Science Laboratories, Inc., State College, Pennsylvania) is a porous polymer based on 2,6-diphenyl-p-phenylene oxide (37). Several investigators have reported on the use of Tenax cartridges as air sampling devices, and specifically for the collection of ambient hydrocarbons (38,39,40). Based on the work of Humrickhouse (41), it was decided that Tenax-GC could be used as a collection medium for the hydrocarbon samples collected during the Washington field study for the following reasons: (1) excellent quantitative and qualitative agreement between Tenax-collected samples and canister samples for alpha-pinene; (2) ease of sample handling; (3) excellent storage stability of up to 10 days with no special storage conditions necessary. These characteristics would allow samples to be collected in Seattle and returned to Pullman for analysis.

The Tenax samples were analyzed in the following manner. Each tube was placed in a tube furnace and heated to 250°C to desorb the sample. The tube was flushed with at least 70 cm^3 of ultra-pure nitrogen which had passed through a cold trap similar to the enrichment loop described above. The desorbed sample was then transferred to an enrichment loop connected to a Perkin Elmer 990 gas chromatograph equipped with a SE-30 glass capillary column (J and W Scientific) and a flame ionization detector. Good separation of the terpene was accomplished with a temperature program of -50°C to 80°C at 4°C/min.

Needle (Leaf) Oil Extraction and Analysis Procedures

A small branch was removed from the tree in the vicinity of the branch that was used for sampling volatile emissions. The cut vegetation was placed in a plastic bag and immediately transported to the field laboratory in Lancaster, PA. Upon arrival at the laboratory, a portion (~5 g) of the needles or leaves was stripped from the woody section of the branch and quickly frozen in a mortar dish containing liquid nitrogen. The vegetation was crushed to a fine powder at liquid nitrogen temperature and then transferred to a Soxhlet extraction apparatus. The crushed vegetation was extracted for six hours with carbon disulfide. The extract was concentrated to a volume of about 5 ml by distilling off most of the carbon disulfide. The concentrate was then sealed in a small vial and returned to our laboratory in Pullman, WA for GC and GC-MS analysis.

Aliquots of the needle oil concentrate were injected into a Hewlett Packard 5840 gas chromatograph equipped with a 30 meter SE-30 glass capillary column and flame ionization detector. Peak quantitation was provided by the HP 5840's computerized data system. The identity of unknown peaks in the GC-FID chromatograms was established by GC-MS. Tentative identifications were made on the basis of mass fragmentation patterns. Structural confirmation was achieved by comparing the fragmentation patterns and retention times with authentic terpene standards.

SECTION 4

NATURAL HYDROCARBON INVENTORY FOR PENNSYLVANIA

A goal of this phase of the program was to determine the types and magnitude of natural hydrocarbons emitted by vegetation in the state of Pennsylvania. This emissions information can be used as input data for a regional air quality model. Two distinct steps are involved in establishing an emission inventory. Hydrocarbon emission rates must be established for major vegetation species in the study area. These measured emission rates are then combined with estimates of regional biomass to arrive at the desired emissions inventory. Vegetation in the Pennsylvania sampling area could best be divided into four categories based on the magnitude and composition of volatile emissions. The four groups are: isoprene emitting hardwoods, non-isoprene emitting hardwoods, monoterpene emitting softwoods and agricultural crops.

Isoprene Emitting Hardwoods

The seven species of deciduous trees studied in this group include: black locust, sycamore, and five species of oak. The category is characterized by a volatile emission with isoprene as its major component. During the field project 19 enclosure samples were collected from this group of trees. As shown in Table 2, measured hydrocarbon emission rates varied from a low of 0.4 µg/g-hr to a high of 58.9 µg/g-hr. The isoprene content averaged 78% of the total hydrocarbon emission. Several compounds with gas chromatographic retention times approximately equal to the monoterpenes accounted for the

TABLE 2. HYDROCARBON EMISSION RATES AND ISOPRENE CONTENT FOR ISOPRENE-EMITTING HARDWOODS

Species	Sampling Date	Time (EST)	Total Emission[1]	%Isoprene	Temperature[2]
White oak	7/30	1210	8.9	91	25.5
	8/8	1338	2.5	40	28.3
Black oak	8/3	1446	3.4	73	23.3
	8/20	1237	48.2	99	34.4
Chestnut oak	8/7	1217	3.8	82	23.3
	8/14	1200	6.0	75	26.1
Same tree	8/14	1229	7.3	75	23.9
	8/14	1303	0.9	82	21.7
	8/16	0600	0.4	70	11.1
Same tree	8/16	1002	1.5	85	16.7
	8/16	1353	1.6	82	20.0
	8/16	1745	1.0	83	17.2
Scarlet oak	8/8	1044	23.5	86	28.9
	8/21	1431	5.7	81	21.1
Red oak	8/21	1338	9.0	77	26.7
	8/22	1400	19.8	86	30.6
Black locust	8/9	1114	12.2	62	27.8
	8/20	1306	17.8	81	28.9
Sycamore	8/22	1001	58.9	78	32.2

[1] μg/g - hr

[2] Enclosure temperature (°C)

remaining 22% of the volatile emission. Positive identification of these compounds was not attempted because of their low concentration. Figure 6 shows a chromatogram typical of this group.

Factors that are suspected of affecting emission rates include: temperature, sunlight, season and species. Volatile emission samples were collected in a manner that would provide as wide a range of these variables as possible. Diurnal emission rate variations were measured by a set of four samples collected from one tree every four hours beginning at 0645. The lowest emission rate (0.4 μg/g-hr) was measured early in the morning when sunlight intensity and the ambient temperatures were low. The emission rate increased by about a factor of 4 during the midday period as shown in Table 2 for chestnut oak on August 16.

Temperature appears to be the variable that best correlates with emission rates. A good linear relationship exists between sample temperature and the logarithm of the emission rate ($\ln Q = a + bT$ or $Q = a'e^{bT}$ where Q is emission rate and T is temperature). This regression has a correlation coefficient of 0.81; the correlation between temperature and emission rate is illustrated in Figure 7. These data suggest that the release of hydrocarbons from this group of trees is strongly related to temperature with approximately 90% of the variation in emission rates associated with temperature variations.

A relationship between temperature and emission rate from isoprene emitting species is supported by other work conducted at Washington State University (42). During 1978-79 monthly samples were collected from a red oak tree to assess the seasonal variation in emission rates. These data show a similar exponential relationship between temperature and emission rate. Results of the Pullman studies are included in Figure 7. The excellent agreement

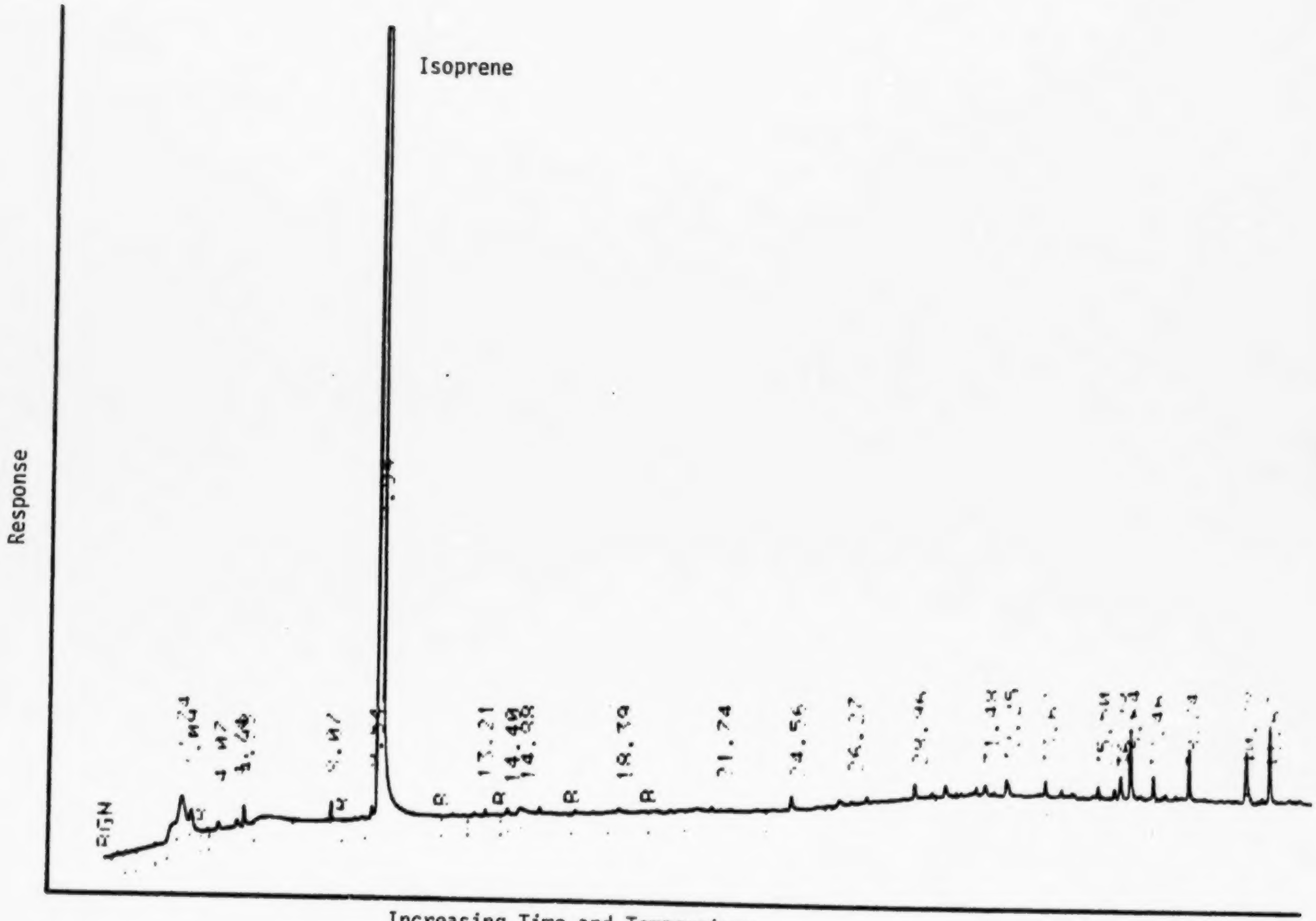


Figure 6. Scarlet oak emission sample chromatogram.

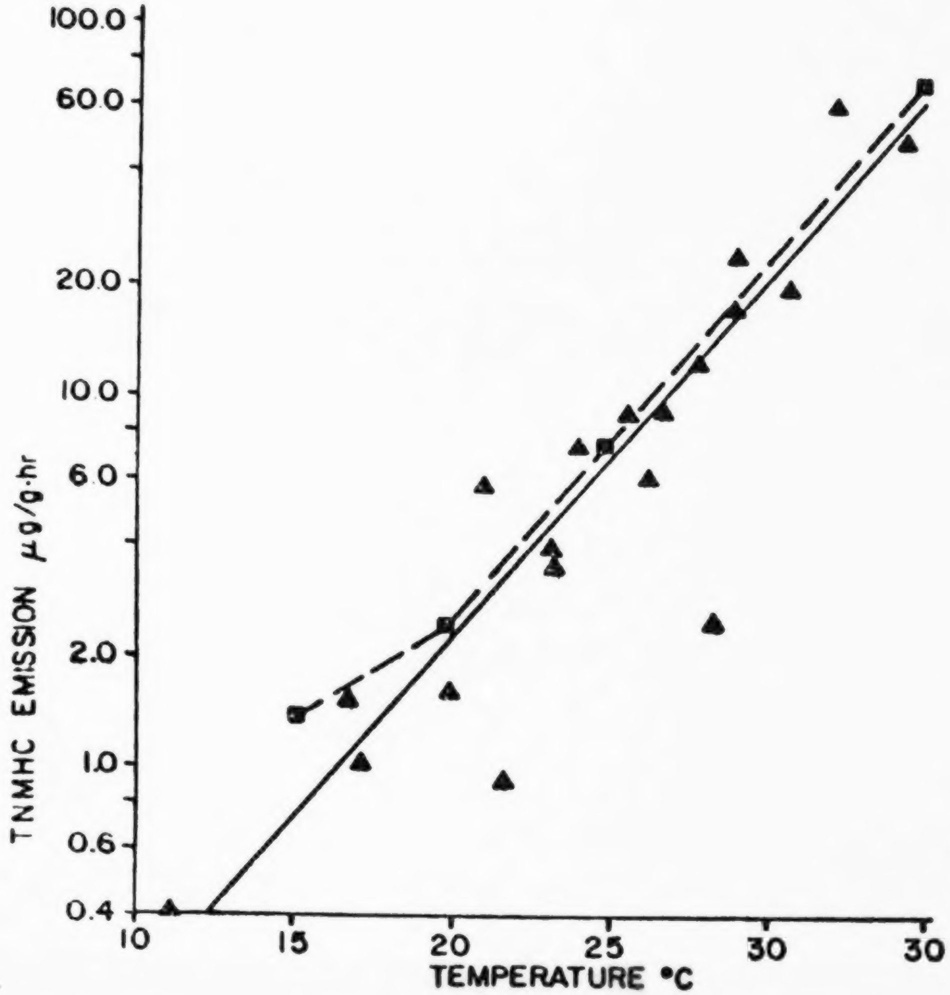


Figure 7. Total non-methane hydrocarbon emission rate as a function of temperature for isoprene emitting hardwoods. Solid line from Pennsylvania study; dashed line from Pullman, Washington samples (42).

between these two studies suggest that the emission rates for isoprene emitting trees can be correlated with temperature, and the results applied to areas having large differences in climate, season, and location.

Non-Isoprene Emitting Hardwoods

The ten species of deciduous trees studied in this group include: black gum, sassafras, tulip, red maple, dogwood, red hickory, black cherry, beech, silver maple and birch. The emissions from this group of trees contained very little or no isoprene. During the field project, 12 enclosure samples from species in this group were collected. Measured hydrocarbon emission rates (Table 3) varied from a low of 0.6 μg/g-hr to a high of 7.8 μg/g-hr. The major emissions in this group appear to be monoterpenes. However, a large number of minor peaks show up in chromatograms (Figure 8) obtained from trees in this category.

The total emission rate from this category also strongly depended upon temperature in an exponential fashion ($r = 0.88$). Figure 9 illustrates this correlation. These data suggest that hydrocarbons are emitted from this group of trees as a result of a temperature dependent process with approximately 91% of the variation in emission rates associated with thermal variations. For comparative purposes, Figure 9 also contains the relationship found for isoprene emitting hardwoods. Both groups exhibit similar emission rate increases with temperature. However, at any given temperature the non-isoprene emitting species show an emission rate approximately 50% lower than the isoprene emitting species.

Monoterpene Emitting Softwoods

Four species of softwoods were sampled during the field program:

TABLE 3. HYDROCARBON EMISSION RATES FOR NON-ISOPRENE EMITTING HARDWOODS

Species	Date	Time (EST)	Total[1] Emission	Temperature[2]
Black gum	7/31	1333	5.8	28.9
Sassafras	7/31	1445	7.3	29.4
Tulip tree	8/2	1513	0.6	18.9
Red maple	8/7	1306	2.1	24.4
Dogwood	8/8	1249	7.8	27.8
Red hickory	8/3	1414	4.0	25.6
Red hickory	8/9	1221	3.2	24.4
Black cherry	8/13	1139	1.3	19.4
Tulip tree	8/22	1131	4.8	28.9
Beech	8/22	1049	2.3	23.3
Silver maple	8/22	1131	2.2	25.0
Birch	8/7	1350	4.3	23.9

[1] μg/g·hr

[2] Enclosure Temperature (°C)

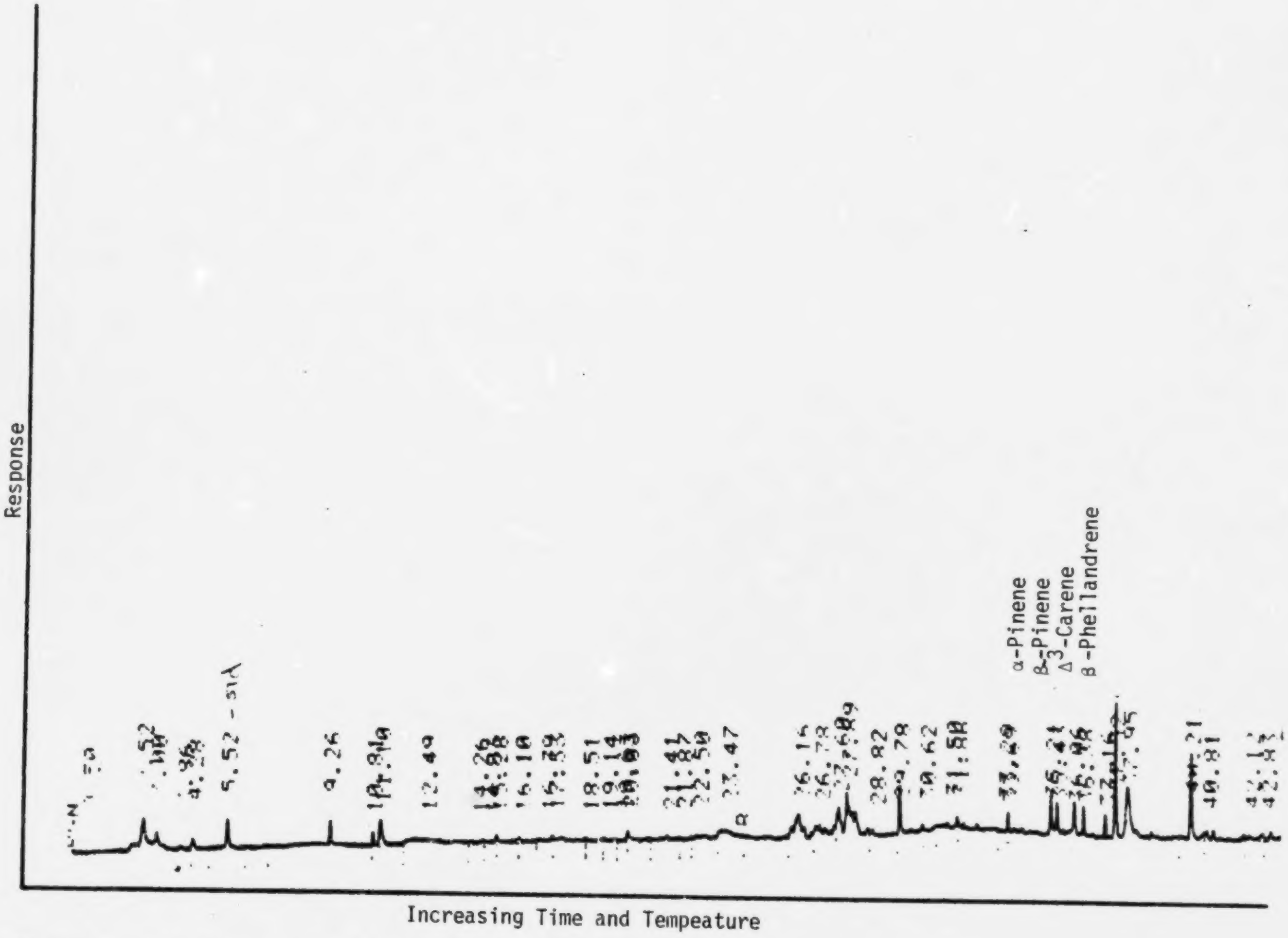


Figure 8. Typical non-isoprene emitting hardwood emission chromatogram.

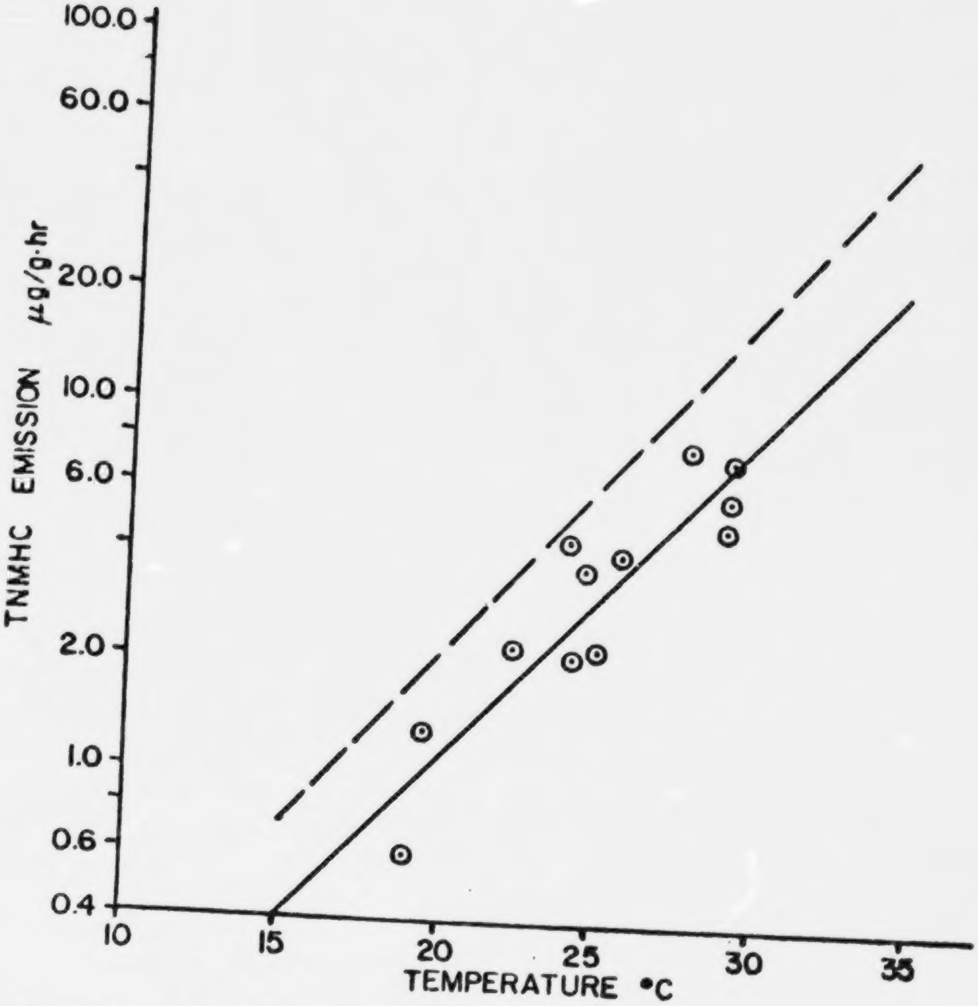


Figure 9. Total non-methane hydrocarbon emission rate as a function of temperature for isoprene and non-isoprene emitting hardwoods. (— — Isoprene emitting hardwoods; ——— Non-isoprene emitting hardwoods.)

eastern hemlock, eastern white pine, Virginia pine, and pitch pine. The group is characterized by a volatile emission that is composed almost entirely of monoterpenes (Figure 10). A total of 11 samples were collected from this group of trees during the field program. As can be seen in Table 4, total hydrocarbon emission rates varied from a low of 1.1 μg/g-hr to a high of 26.5 μg/g-hr.

The emission rates from this group of trees do not correlate with temperature as did the hardwood species. Diurnal emission changes were studied by collecting samples at different time intervals from an eastern white pine as indicated in Table 4.

Agricultural Crops - Included in this group are a variety of agricultural crops important to the state of Pennsylvania. Emission rate measurements (Table 5) were made on corn (2.0 μg/g-hr), tobacco (0.3 μg/g-hr), alfalfa (35 $\mu g/m^2$-hr), clover (115 $\mu g/m^2$-hr), and mixed forage (346 $\mu g/m^2$-hr). The calculation of emission rates for corn and tobacco and the calculation of emission fluxes for the remaining crops were dictated by the type of enclosure used to collect the sample. The normal bag procedure was used to sample single corn and tobacco plants. A bag fixed to a sealing ring placed on the soil was employed for the other crops. Isoprene was not emitted in significant amounts by any members of the group. Compounds eluting near the monoterpenes appear to be the major emission components. In all cases, individual compound concentrations were very low and consequently identification of individual species was not attempted. More data are needed before any conclusions can be made on the magnitude and variations in emissions from this group.

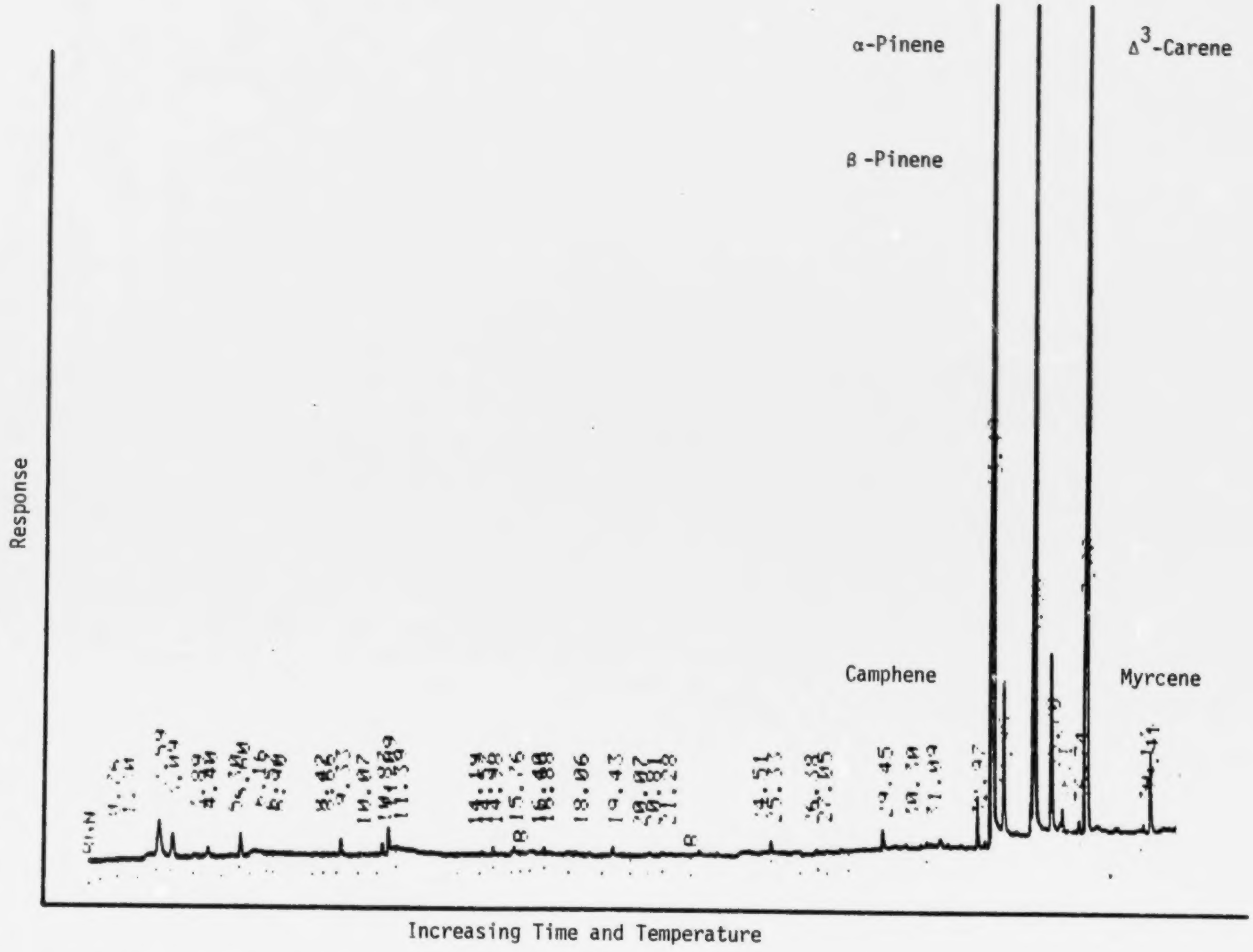


Figure 10. Virginia pine emission sample chromatogram.

TABLE 4. HYDROCARBON EMISSION RATES FROM MONOTERPENE EMITTING SOFTWOODS

Species	Date	Time (EST)	Total[1] Emission	Temperature[2]
Eastern hemlock	8/2	1428	1.1	18.9
Eastern hemlock	8/13	1320	1.5	20.0
Eastern white pine	8/6	0557	3.9	21.7)
Eastern white pine	8/6	0957	2.9	30.6} Same tree
Eastern white pine	8/6	1422	3.0	27.8)
Virginia pine	8/20	1338	7.2	28.3
Pitch pine	8/23	1218	10.7	23.9
Eastern white pine	8/17	1028	12.8	23.3)
Eastern white pine	8/17	1107	26.5	18.3} Same tree
Eastern white pine	8/17	1133	4.0	19.4)

[1] μg/g-hr
[2] Enclosure Temperature (°C)

TABLE 5. HYDROCARBON EMISSION RATES FOR AGRICULTURAL CROPS

Sample	Date	Time (EST)	Emission Rate	Temperature, °C
Corn	8/10	0606	2.4[2]	21.7
Corn	8/10	0946	1.3[2]	33.3
Corn	8/10	1347	2.3[2]	35.0
Tobacco #1	8/15	1049	0.3[2]	21.1
Tobacco #2	8/15	1121	0.4[2]	22.8
Forage[1]	8/15	1205	346[3]	25.6
Alfalfa	8/23	1003	35[3]	23.9
Clover	8/23	1104	115[3]	25.0

[1] red clover, dandelion, broom grass
[2] µg/g-hr
[3] $\mu g/m^2$-hr

SECTION 5

BIOGENIC HYDROCARBON INVENTORIES

1. York County Sampling

The empirical relationships developed in the previous sections of this study allow the estimation of hydrocarbon emission rates from a knowledge of tree species and forest temperature. These emission estimates can be combined with a forest survey and leaf biomass relationships to obtain an inventory of the biogenic hydrocarbon emissions from a forested area. The details of this inventorying procedure will be illustrated by determining the magnitude of hydrocarbon emissions from the hardwood forest surrounding the sampling site in York County, Pennsylvania.

The first step in developing an emission inventory is to determine the species, size, and number of trees present in the study area. These data were obtained for us by Dr. Parks, Millersville State College. The complete forest survey results are given in Appendix 1. Table 6 provides a summary of the survey data for the non-isoprene emitting species while Table 7 lists the same information for the isoprene emitting species. These tables contain the frequency and diameter at breast height (DBH) for the 14 hardwood species found in the study forest. In each case the data are presented for young trees which form the understory of the forest and mature trees which form the overstory. There were no softwood trees present in the study forest.

The second step in developing an emission inventory is to determine the total leaf biomass of the study area. A widely used method for estimating

TABLE 6. FOREST SURVEY DATA FOR NON-ISOPRENE EMITTING HARDWOODS

Species	Canopy Position	Frequency trees/ha	Ave DBH cm	Leaf Biomass kg/tree	Species Total
Tulip tree	overstory	16.62	48.57	29.26	486.30
	understory	4.78	7.69	1.29	6.16
Red maple	overstory	10.39	37.07	18.51	192.32
	understory	62.39	11.53	2.56	159.72
Black gum	overstory	2.07	19.46	6.21	12.85
	understory	81.64	7.96	1.36	111.03
Birch	overstory	8.29	34.35	16.26	134.79
	understory	62.40	16.13	4.52	282.05
Black cherry	overstory	2.07	46.01	26.69	55.25
	understory	4.78	26.42	10.42	49.81
Sassafras	overstory	0.0	0.0	0.0	0.0
	understory	81.64	17.60	5.24	427.79
Dogwood	overstory	0.0	0.0	0.0	0.0
	understory	120.01	6.81	1.05	126.01
Hickory	overstory	0.0	0.0	0.0	0.0
	understory	9.62	7.69	1.29	12.41
Chestnut	overstory	0.0	0.0	0.0	0.0
	understory	14.40	5.96	0.84	12.10

Forest Total = 2069 kg/ha
= 206 g/m^2

TABLE 7. FOREST SURVEY DATA FOR ISOPRENE EMITTING HARDWOODS

Species	Canopy Position	Frequency trees/ha	Ave DBH cm	Leaf Biomass kg/tree	Species Total kg/ha
Black oak	overstory	99.66	33.49	15.58	1552.70
	understory	14.40	23.91	8.80	126.72
Chestnut oak	overstory	41.53	31.08	13.73	570.21
	understory	72.02	13.14	3.19	229.74
Black locust	overstory	16.62	32.61	14.89	247.47
	understory	14.40	13.32	3.26	46.94
Scarlet oak	overstory	24.92	36.65	17.32	431.61
	understory	0.0	0.0	0.0	0.0
White oak	overstory	26.98	31.89	14.34	386.89
	understory	33.59	19.11	6.02	202.20

Forest Total = 3794 kg/ha
= 379 g/m^2

this parameter relies upon regression equations relating biomass to a more easily measured dimension of the tree. These regressions are based on the principle that tree dimensions will maintain their functional balance as they enlarge. However, the enlargement will not maintain constant ratios between the dimensions. Consequently, the relationship between height and diameter is expressed in a general equation as $y = ax^b$.

These exponential relationships that characterize harmonious growth with changing proportions are termed allometric. Allometric equations are developed by cutting down a number of sample trees and subjecting them to intensive measurements. The literature contains four allometric relationships between DBH and leaf biomass that are of interest to this study. A graph of these relationships is given in Figure 11. The first relationship was developed by Whittaker et al. (43) from three deciduous tree species in New Hampshire. Relationship #2 was reported by C. D. Monk et al. (44) from an oak-hickory community in Georgia. The third relationship was developed by R. H. Whittaker (45) from a conifer and deciduous forest on Long Island, New York. The last relationship was reported by Sollins et al. (35) from data collected from 40 tree species in the southeastern U.S.

The relationship developed by Sollins was chosen for estimating leaf biomass at the Pennsylvania study site. This decision was based on the following considerations: (1) Relationship #1 results in the lowest biomass values and could therefore bias the results. (2) There is a discrepancy between the slope of relationship 2 and the remaining studies suggesting that the data were collected from widely different forest communities. (3) The agreement between the relationship developed in New York, and the one established in the southeastern U.S., suggest that these two relationships could be applied to

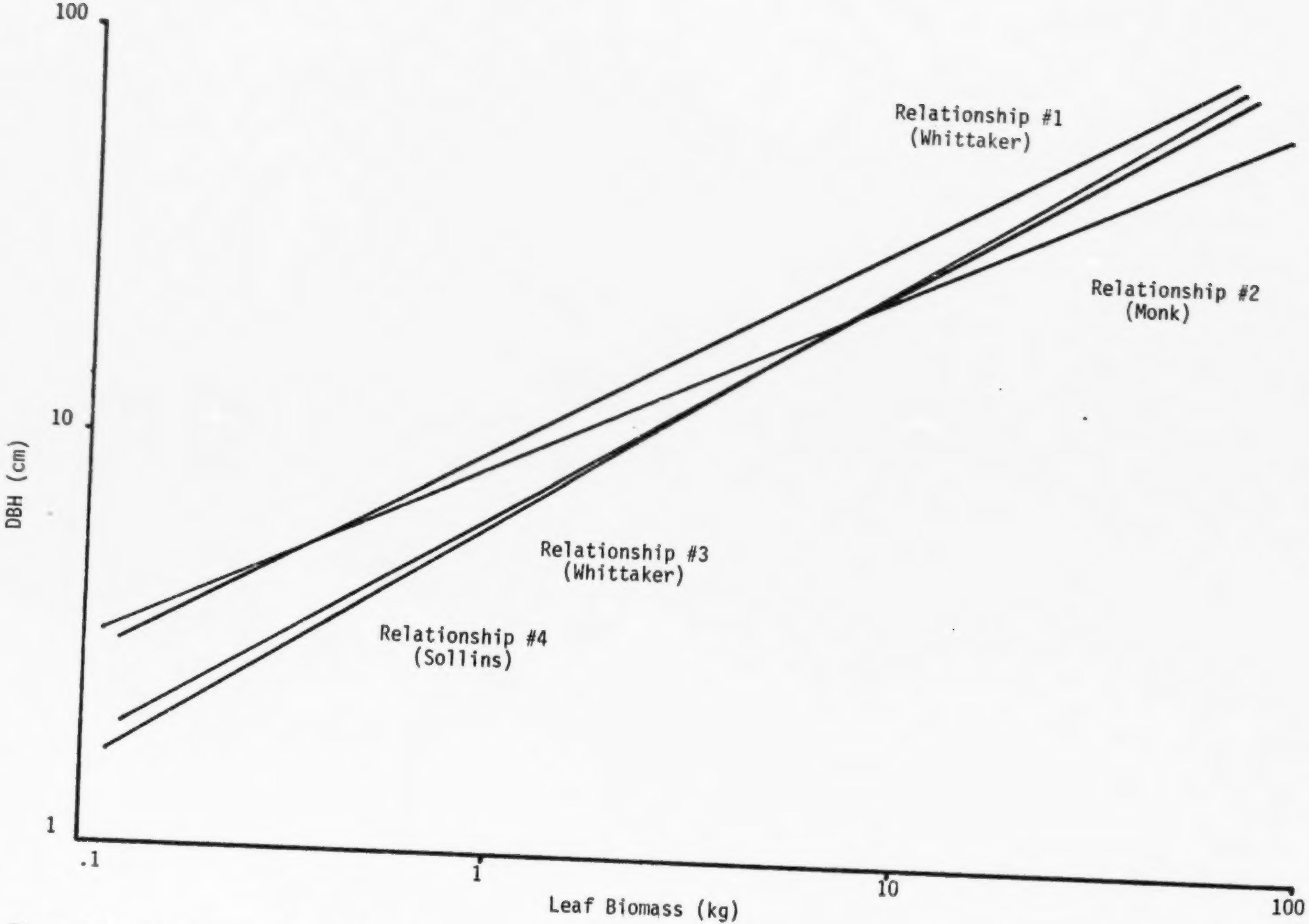


Figure 11. Comparison of four allometric relationships for determination of leaf biomass.

Pennsylvania. (4) Relationship #4 was based upon the largest data base.

The Sollins relationship was derived from extant dry-weight data collected from about 40 conifer and deciduous species in the southeastern U.S. including 250 trees with DBH >10 cm. The equation was adjusted to remove the bias inherent in logarithmic transformation of data in regression analysis. The transformed equation is:

$$L = 0.0411\ D^{1.695}$$

L = leaf biomass (kg)

D = Diameter at breast height (cm)

This allometric relationship was used in conjunction with the average DBH to obtain the leaf biomass reported in column 5 of Tables 6 and 7. Leaf biomass was then multiplied by the tree frequency to obtain the total leaf biomass of each species (column 6). The summation of the species leaf biomass results in the total leaf biomass per unit area.

The biogenic hydrocarbon emission flux was estimated by multiplying the biomass value (g/m^2) by the emission rate ($\mu g/g\text{-}hr$). Hydrocarbon emission rate values were derived from the regressions developed for the four vegetation groups discussed previously. Figure 12 presents the flux ($\mu g/m^2\text{-}hr$) of hydrocarbons and isoprene from the York County forest as a function of temperature. It should be noted that the biomass factors available from the regression relationships in Figure 11 vary by approximately ± 30% relative to the relationship from Sollins which was used to calculate the emission fluxes in this inventory.

2. Pennsylvania Inventory

The development of a biogenic hydrocarbon inventory for Pennsylvania

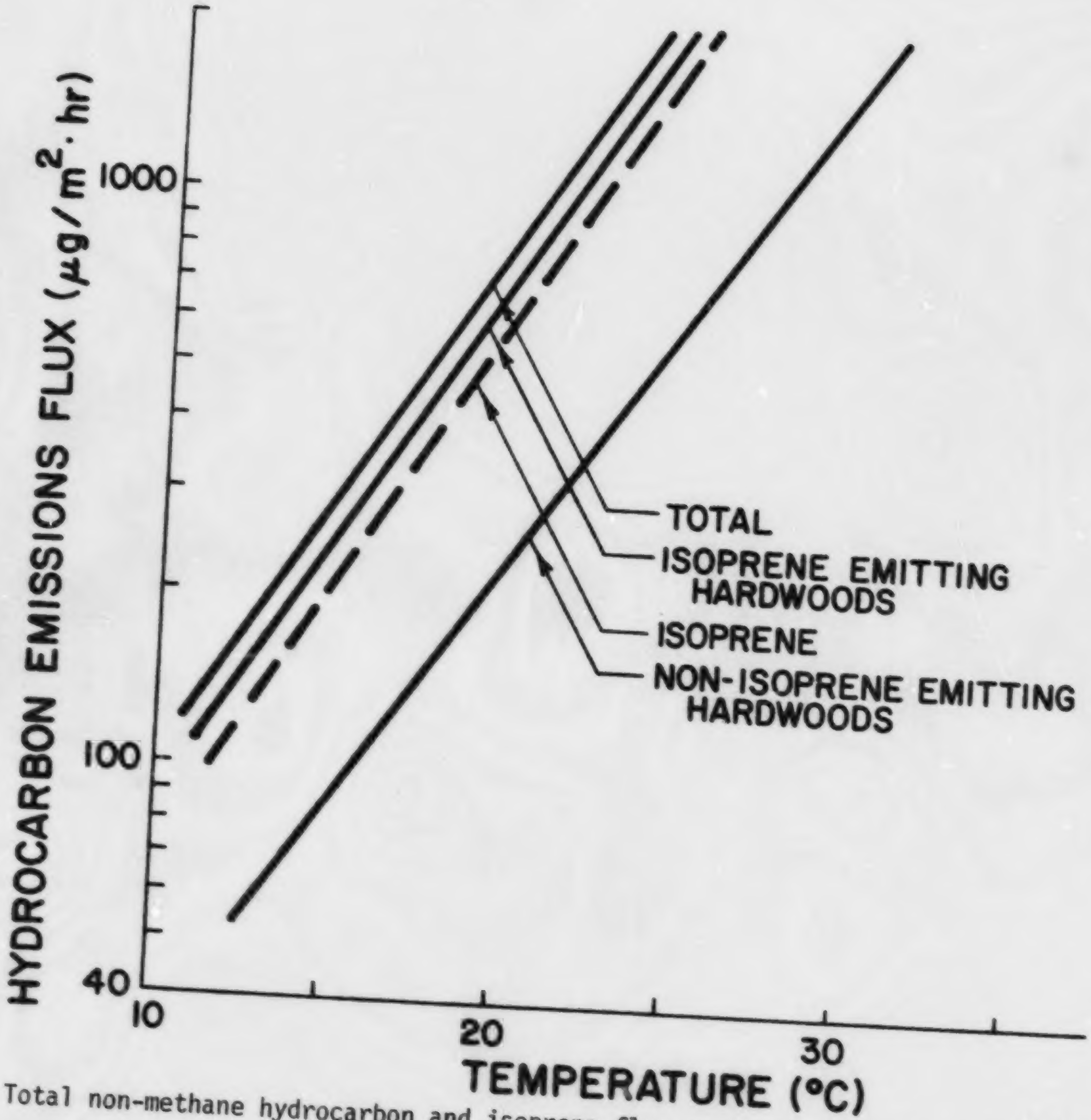


Figure 12. Total non-methane hydrocarbon and isoprene flux vs temperature for Pennsylvania study site.

utilizes the same principles as that described for the York County study area. Forest data for the inventory were obtained from a preliminary U.S. Forest Service survey (46) of Pennsylvania's commercial forests (95% of all forested land). This survey lists the frequency of tree species by DBH class, for eight regions of the state. A map of these eight forest regions is shown in Figure 13. From this raw data the frequency of non-isoprene emitting hardwoods, isoprene emitting hardwoods, and monoterpene emitting softwoods was determined. Table 8 provides a listing of the number of trees in each of 10 DBH classes.

The mid-point of each DBH class was used to determine the leaf biomass of an average tree in each class using the allometric relationship of Sollins. The total leaf biomass for the state was obtained from the summation of the products of the tree frequency and average leaf biomass for each DBH class. This calculation is summarized in Table 9.

The magnitude of hydrocarbons emitted from Pennsylvania's forests can now be determined by multiplying the total leaf biomass for each of the three tree groups by an emission rate. Emission rates from hardwoods were determined from the observed relationship with temperature using average August temperatures as shown in Table 10. Since there is no similar strong relationship between temperature and emission rates from softwoods, representative daytime and nighttime values from the enclosure sampling program were assumed as indicated in Table 11.

A summary of the calculations required to obtain an estimate of hydrocarbon emission from forests is contained in Table 11. As this table shows, approximately 2500 tons/day of hydrocarbons are emitted by Pennsylvania's commercial forests during August. Isoprene is the largest component and is responsible for 25% of the forest emission.

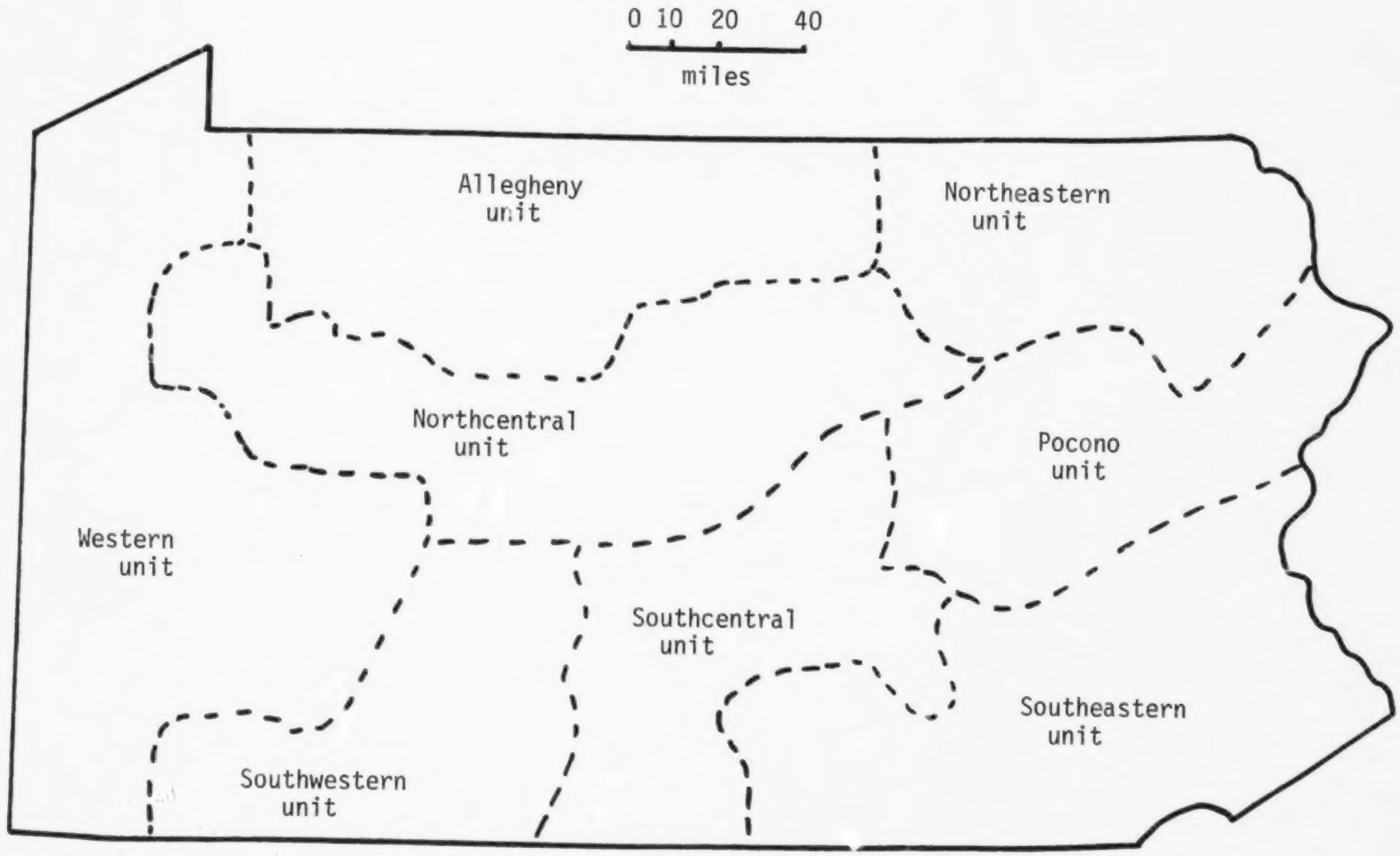

0 10 20 40
miles
Allegheny unit
Northeastern unit
Northcentral unit
Pocono unit
Western unit
Southcentral unit
Southeastern unit
Southwestern unit

Figure 13. Map showing Pennsylvania forest regions.

TABLE 8. TREE FREQUENCY BY DIAMETER CLASS (THOUSANDS OF TREES) IN PENNSYLVANIA COMMERICAL FORESTS

Region		Diameter class (inches at breast height) 5.0-6.9	7.0-8.9	9.0-10.9	11.0-12.9	13.0-14.9	15.0-16.9	17.0-18.9	19.0-20.9	21.0-28.9	29+
South eastern	I[1]	18088	14006	10941	8235	5500	3216	2048	743	1041	37
	N[2]	19382	13986	7451	5866	3666	2391	1286	550	957	162
	C[3]	4038	2084	1519	708	438	152	56	19	13	0
Pocono	I	39177	33336	19411	9651	4669	2366	1174	532	531	7
	N	50259	21331	10596	4633	2211	724	638	206	86	0
	C	10035	5038	3446	3159	731	595	348	127	222	19
South central	I	27344	23911	21646	12840	7878	4346	2824	1339	1439	78
	N	33281	18290	9822	5939	3067	1827	880	508	419	46
	C	10327	6578	3308	1691	428	256	273	104	78	7
South western	I	27046	24752	17248	8964	5109	2964	1469	830	976	60
	N	38659	23469	12767	8740	4817	2222	1069	783	531	39
	C	3024	2253	1867	970	345	271	106	79	32	
North central	I	47996	37528	24675	16652	10250	5175	3209	1512	1240	116
	N	71696	42501	26631	13778	7215	3589	1913	619	564	50
	C	21195	10740	6757	4146	2247	1364	895	314	486	35
North eastern	I	12224	10550	8800	4098	1691	757	217	283	234	7
	N	51599	33771	20525	10330	4624	2003	926	315	362	37
	C	9864	5138	4491	3133	1556	936	292	142	190	19
Allegheny	I	22536	20567	16770	9643	6011	2926	2303	916	945	53
	N	145086	116798	73295	38975	22341	10551	5164	2570	1750	130
	C	20632	10580	3596	2628	1404	1128	452	441	408	8
Western	I	17809	16162	9705	6248	3100	2458	1627	935	1058	318
	N	61472	37286	27480	15713	8387	5374	3193	1381	2045	160
	C	13832	6721	4072	1426	323	171	84	59	27	0

[1] Isoprene emitting hardwood
[2] Non-isoprene emitting hardwood
[3] Conifer (monoterpene emitting softwood)

TABLE 9. TOTAL LEAF BIOMASS IN PENNSYLVANIA COMMERCIAL FORESTS

Diameter Class (cm)	Total Tree Frequency x 1000			Leaf Biomass/Tree (x 10^3 g)	Total Leaf Biomass (g x 10^{10})		
	Isoprene	Non-Isoprene	Conifer		Isoprene	Non-Isoprene	Conifer
1.9-2.9[1]	56205	102566	2188398	0.40	2.3	4.1	87.5
3.0-4.9[1]	50203	91612	1050340	2.09	10.5	19.1	219.5
5.0-6.9	212220	47434	92947	4.16	88.3	196.1	38.7
7.0-8.9	180812	307432	49132	6.77	122.4	208.1	33.3
9.0-10.9	129196	188567	29056	9.89	127.8	186.5	28.7
11.0-12.9	76331	193974	17861	13.47	102.8	261.3	24.1
13.0-14.9	44208	56329	7472	17.49	77.3	98.5	13.1
15.0-16.9	24208	28681	4873	21.93	53.1	62.9	10.7
17.0-18.9	14871	15069	2506	26.77	39.8	40.3	6.7
19.0=20.9	7090	6932	1285	32.01	22.7	22.2	4.1
21.0-28.9	7437	5362	1456	46.72	34.7	25.0	6.8
29+	676	624	88	63.64	4.3	3.9	0.6
				TOTAL	686.0	1128.2	473.7

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[1] These data were available for the entire state only; all other classes were tabulated initially by region as shown in Figure 13.

TABLE 10. AVERAGE METEOROLOGICAL CONDITIONS

Average daytime temperature[1]	27 °C
Average nighttime temperature[1]	18 °C
Hours of sunlight[1]	12.5 hr

[1] Average August values from Climatic Atlas of the United States, U.S. Department of Commerce, Environmental Science Services Administration, June 1968.

TABLE 11. HYDROCARBON EMISSIONS FROM PENNSYLVANIA FORESTS

Emission Type	Emission Rate μg/g hr	Emission Duration (hrs)	Biomass 10^{10} g	Total Emission Tons/day
Isoprene Emitting Species				
daytime (NMHC)	9.37	12.5	686	803
nighttime (NMHC)	1.36	11.5	686	84
Isoprene	7.31	12.5	686	626
Non-Isoprene Emitting Species				
daytime (NMHC)	4.39	12.5	1128	619
nighttime (NMHC)	0.71	11.5	1128	92
Conifer Species				
daytime (NMHC)	6.9	12.5	474	408
nighttime (NMHC)	9.2	11.5	474	501

Total Forest Hydrocarbon Emissions = 2510 tons/day

The 1974 agricultural census reports the three major crops in Pennsylvania as corn, pasture and hay (47). These three crops account for 82% of the non-forest land. An estimate of the hydrocarbon emissions from these croplands can be calculated by using the measured emission rates reported in an earlier section of this report. The calculations involved in this estimate are summarized in Table 12. These calculations indicate that 890 tons/day will be emitted by agricultural lands during August and corn is the major emitter.

Table 13 summarizes the hydrocarbon emissions from Pennsylvania by land class. As this table indicates, 70% of the total land area of Pennsylvania was included in this inventory. The largest section (23%) of the land not included in the inventory consisted of swamplands, industrial and urban areas, and areas classified as water by resource evaluation standards, but defined as land by the Bureau of Census. Vegetation in this land classification would be less dense than in the forest or cropland classification, and would therefore contribute a smaller amount of hydrocarbons to the total emissions. Similarly, pasture and other croplands were not included. Because of the omission of the land areas, this study will underestimate the total hydrocarbon emissions from Pennsylvania.

A total of 3400 tons/day of natural hydrocarbons are emitted during August from Pennsylvania, for an average state-wide emission rate of 1660 $\mu g/m^2$-hr. This emission estimate was made from the extrapolation of forest and agricultural data collected in southeastern Pennsylvania. The extrapolation of the forest emission data should provide a relatively accurate estimate of forest emissions. There were a reasonable number of samples obtained from trees, the results showed good agreement with previous work, and

TABLE 12. HYDROCARBON EMISSIONS FROM PENNSYLVANIA CROPLANDS

Crop	Emission Rate	Area m^2 x 10^9	Conversion g/m^2	Biomass g x 10^{10}	Emission Tons/day
Pasture	346 μg/m^2·hr	4.14[1]	---	---	34
Corn	2.0 μg/g·hr	5.61[1]	3138[1,2]	1760	844
Tobacco	0.3 μg/g·hr	0.04[1]	185[1]	0.74	0.1
Hay	75 μg/m^2·hr	6.52[1]	---		12

TOTAL EMISSION = 890 Ton/day

[1] U.S. Agricultural Census 1974 wet weight; [2] 1570 g/m^2 dry weight.

TABLE 13. BIOGENIC HYDROCARBON EMISSION INVENTORY FOR PENNSYLVANIA IN 1979

Land Class	Area m^2 x 10^{10}	% Land Area	Emissions Tons/day
Forest Land			
Commercial	6.44	55	2507
Urban	0.03	<1	
Unproductive	0.12	1	
Productive reserved	0.22	2	
Non-Forest Land			
Corn, Tobacco, hay[a]	1.22	10	856
Pasture	.41	4	34
Other cropland[a]	0.35	3	
Other[b]	2.69	23	
TOTAL	11.65		3397 tons/day

[a] Source: Census of Agriculture, less croplands used only for pasture.
[b] Includes swampland, industrial and urban areas, other non-forest land, and land classed as water by Resources Evaluation Standards, but defined by the Bureau of the Census as land.

the forest biomass data were very detailed. However, hydrocarbon emissions from agricultural crops are not as well documented, and the emission estimates from these data could thus involve a significant error. Very little is known about hydrocarbon emissions from crops. There is no available data concerning the effects of temperature, sunlight, or season upon emissions from crops. In any case, an extrapolation of this magnitude can only provide a rough estimate of biogenic hydrocarbon emissions.

SECTION 6

ESSENTIAL OIL EXTRACTION STUDIES

In order to gain some additional insight into the processes that control hydrocarbon emissions from vegetation, we determined the monoterpene composition of the leaves (needles) and woody tissue in most of the tree species sampled for volatile emissions. Thus we were able to compare the monoterpene composition within the vegetation with the hydrocarbon composition of emission samples. If simple volatilization of the leaf and branch oleoresin constituted the primary release mechanism for hydrocarbons, the composition of the volatile emissions should be similar to the composition of the leaf and branch oils.

Monoterpene Emitting Softwood Species. It has been reported that the release of monoterpenes is dependent on the physical properties of the system (11). If the source of the volatile hydrocarbon emissions from conifers is the needle oil or oleoresin, the composition of the volatile emissions should be similar to the composition of the needle and branch oils. Table 14 shows that needle and branch extracts did indeed correspond closely with the volatile emissions.

The similarities in the composition of the extract samples and volatile emissions supports the hypothesis that the terpenes are released from the conifers as a result of volatilization. The lack of a correlation between emission rates and temperature requires that the actual release of the hydrocarbons is controlled by some temperature independent process.

A possible explanation would be that during periods of high heat loss the plant closes its stomata to reduce water loss, and as a result prevents the emission of the monoterpenes.

TABLE 14. NEEDLE, BRANCH AND VOLATILE COMPOSITION OF SELECTED CONIFER SPECIES

Species	Compound	%Leaf	%Branch	%Volatile
E. White Pine[1]	2,4-hexadiene-1-ol	4	--	--
	Sabinene	3	61	--
	α-Pinene	36	--	27
	Camphene	5	15	7
	β-Pinene	15	24	22
	Myrcene	25	--	34
	β-Phellandrene	5	--	8
	Δ^3-Carene	8	--	--
	Linalool	<1	<1	5
Virginia Pine	Sabinene	4	<1	--
	α-Pinene	35	37	25
	Camphene	7	<1	6
	β-Pinene	22	24	12
	Myrcene	4	8	4
	Δ^3-Carene	29	31	18
	Unidentified			35

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[1] The % volatile is the average of seven samples and therefore does not add up to 100%.

Isoprene Emitting Hardwood Species. Samples of the leaf and branches of each tree sampled were collected and later prepared for GC/MS analysis by crushing and extracting with carbon disulfide. Eight compounds were identified as the major components of the leaf and branch extracts. The identified compounds are: α-pinene, myrcene, camphene, 2,4-hexadiene-1-ol, methyl salicylate, 3-hexene-1-ol, benzyl alcohol and an unknown $C_6H_{10}O$ compound. Several higher molecular weight (C_{15}) compounds were observed in the extracted samples. These heavier compounds were not identified or accounted for in the compositions since they are considered to be insignificant in the volatile emissions. Isoprene was not detected in any of the extracted samples. It was either lost during the solvent evaporation step prior to GC/MS analysis, or it is produced on a nearly instantaneous basis by the plant during the emission process and does not remain in the essential oils.

Table 15 provides a comparison between the composition of the leaf and branch extracts and the volatile emissions. Very few similarities exist between the composition of the extract samples and the volatile emissions. We have recently shown that certain oxygenated compounds exhibit limited stability in the stainless steel sample canisters (48). Alcohols are especially troublesome and consequently could be present in plant emissions but were not detected due to losses in the sampling canisters prior to analysis. There is no apparent relationship between volatile emissions and essential oil content in the isoprene emitting hardwoods.

TABLE 15. LEAF, BRANCH AND VOLATILE COMPOSITION OF ISOPRENE EMITTING HARDWOODS, PENNSYLVANIA, 1979

Species	Compound	% Composition Leaf	 Branch	 Volatile
White oak	2,4-hexadiene-1-ol	44	--	--
	Unknown $C_6H_{10}O$	56	--	--
	Methyl salicylate	<1	18	--
	Isoprene	--	--	90
	Unidentified		82	
Black oak	2,4-hexadiene-1-ol	43	--	--
	3-hexene-1-ol	19	--	--
	Benzyl alcohol	38	--	--
	Isoprene	--	--	73-99
Black locust	α-Pinene	27	--	--
	2,4-hexadiene-1-ol	27	--	--
	Camphene	47	--	--
	Myrcene	--	--	2
	Unknown terpene	--	--	6
	Isoprene	--	--	62-81

SECTION 7

COMPARISON OF ENCLOSURE AND GRADIENT PROFILE METHODS FOR MEASURING BIOGENIC HYDROCARBON EMISSIONS

Emission fluxes were measured during the same time periods by both the enclosure and micrometeorological gradient procedures. Due to the complexity of each of these methods and the assumptions invoked in the calculation of emission fluxes, it is impossible to determine the absolute accuracy of either method. However, if results from the two procedures agree, the measured fluxes would be expected to be reasonably accurate.

Pennsylvania forest. Fourteen profile measurements of the isoprene flux over the forest canopy in Pennsylvania were performed during the period August 7 to August 23, 1979. Three of these tests had to be discarded because the wind direction changed during the sampling period; two tests were not considered because of apparent contamination of the samples with hydrocarbons which eluted at approximately the same time as isoprene.

Insolation measurements recorded during the test periods ranged from near zero to greater than 1.3 Langleys/min, while ambient temperature varied from 18°C to 29°C. All tests were conducted during slightly unstable to unstable conditions as indicated by the observed temperature gradients, while wind speeds were between 0.9 and 4.9 m/s. Typical profiles of wind speed, temperature, and isoprene concentration are shown in Figure 14; the data for all of the profile tests are summarized in Table 16.

The errors involved in the best-fit wind speed and temperature profiles

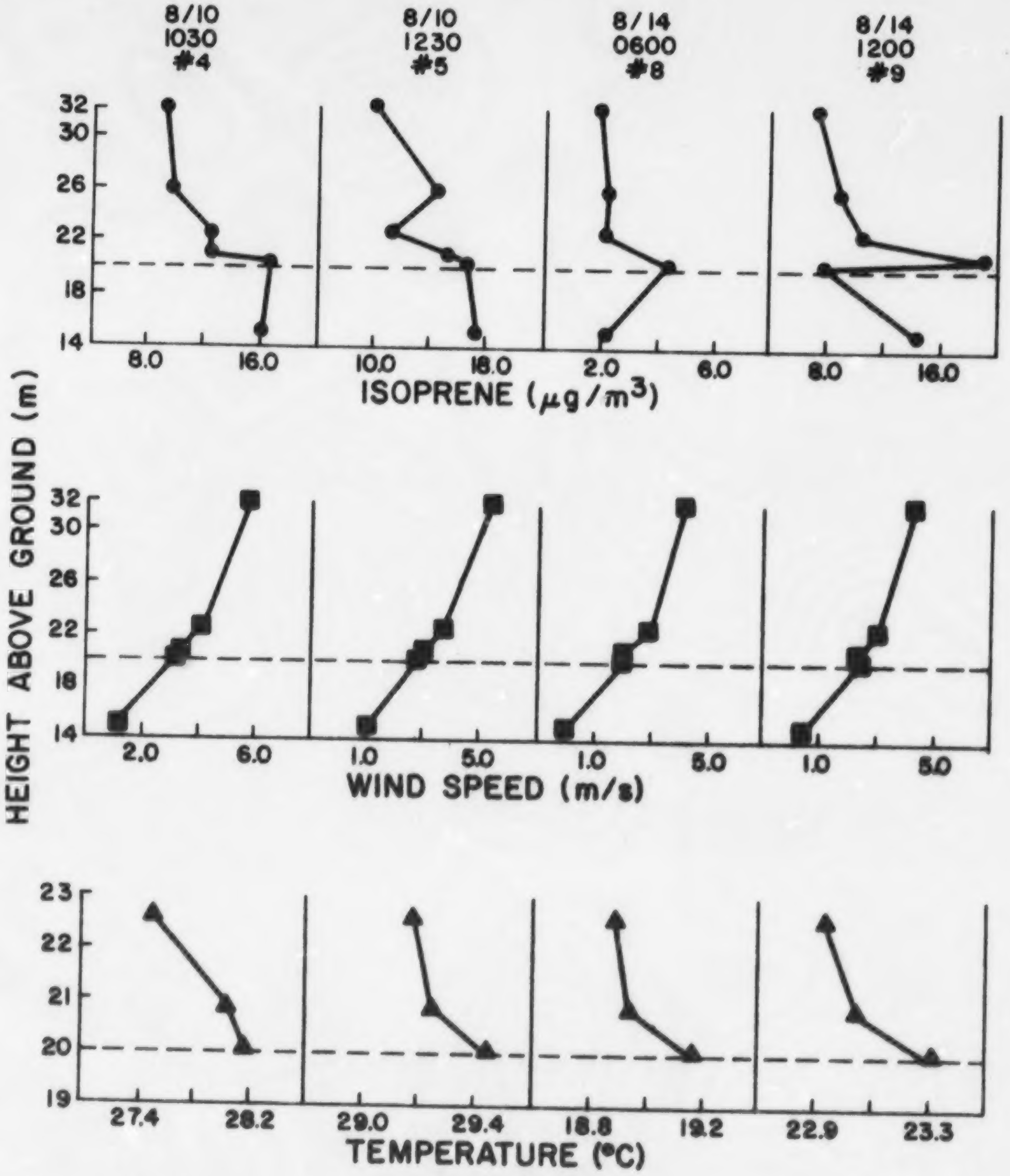

Figure 14. Typical profiles of wind speed, temperature, and isoprene concentration in Pennsylvania.

TABLE 16. ISOPRENE EMISSION FLUXES AND METEOROLOGICAL PARAMETERS FROM GRADIENT PROFILE EXPERIMENTS, PENNSYLVANIA.

Test No.	Date (1979)	Time (EST)	Isoprene Flux* ($\mu g/m^2$-hr)	T_z* (°C)	u_z* (m/s)	σ_θ (34 m) (deg)	Radiation (Ly/min)	Relative Humidity (%)	Heat Flux* (W/m^2)	Monin-Obukhov Length* (m)	e_u (%)	ΔT_o (°C)	ΔT_p (°C)
1	8/7	1330	2,890	23.8	2.1	36	....	60	80	-60	5	-.06	-.06
2	8/9	1600	5,660	25.3	0.9	25	0.4	60	37	-14	18	-.09	-.03
4	8/10	1030	11,200	26.9	4.9	23	1.2	65	373	-155	6	-.17	-.16
5	8/10	1230	6,600	28.9	4.5	24	1.2	61	159	-266	8	-.11	-.08
8	8/14	0600	2,890	18.6	3.7	24	0.1	62	118	-218	13	-.05	-.07
9	8/14	1200	3,860	22.6	3.5	33	0.5	62	149	-151	9	-.11	-.09
10	8/21	1300	2,760	19.2	1.4	38	0.7	76	52	-21	40	-.09	-.04
11	8/22	1130	2,530	22.4	1.7	23	1.3	59	64	-44	9	-.15	-.05
13	8/22	1600	1,610	23.7	1.8	30	0.6	52	113	-30	9	-.08	-.07

* All values determined for 26 m (6 m above the canopy). Relative humidity obtained from a dew point sensor located at 20 m and radiation measured with a sensor located at 2 m in an open area away from the tower.

e_u ≡ mean percent error between observed and predicted (best-fit) wind speeds (at 20, 20.9, 22.6, and 32 m)

ΔT_o ≡ observed temperature gradient between 20.9 m and 22.6 m.

ΔT_p ≡ predicted (best-fit) temperature gradient between 20.9 and 22.6 m.

are also shown in Table 16. The calculated parameters were obtained as outlined previously using a non-linear best-fit technique based upon the measured wind and temperature values. During the calculation process, it was found that the overall mean errors between measured and best-fit profiles (based on four wind speed and three temperature measurement points) could best be minimized by using only wind speeds measured at 20.9 m and 32.0 m and temperatures measured at 20.8 m and 22.6 m in the actual best-fit calculation. When more measurement points were included in the calculation, convergence was not consistently achieved and the mean errors between predicted and observed values at all levels generally increased. As shown in Table 16, the mean errors in the best-fit wind speed profiles were typically less than 10%; the largest mean error was 40% for a test with relatively low wind speeds. The differences in the observed and predicted temperature profiles were also relatively small in most cases. Significant differences did occur in 3 tests, but it should be noted that the calculated isoprene flux is relatively insensitive to these kinds of variations. Calculations of the systematic errors in the technique in Appendix 2 indicate that uncertainties in the temperature profiles have little effect upon the calculated isoprene flux. As a result, those disconcerting differences between the observed and predicted temperature profiles do not appear to be a major source of error in the calculated emission fluxes.

Isoprene concentrations measured at the mid-point of the sampling heights (26 m) averaged 7.8±3.9 $\mu g/m^3$. The isoprene concentration at this level increased with increasing ambient temperature as shown in Figure 15. The calculated flux of isoprene for the nine experiments ranged from 1,610 to 11,200 $\mu g/m^2$-hr with mean and median values of 4440 and 2890 $\mu g/m^2$-hr. The

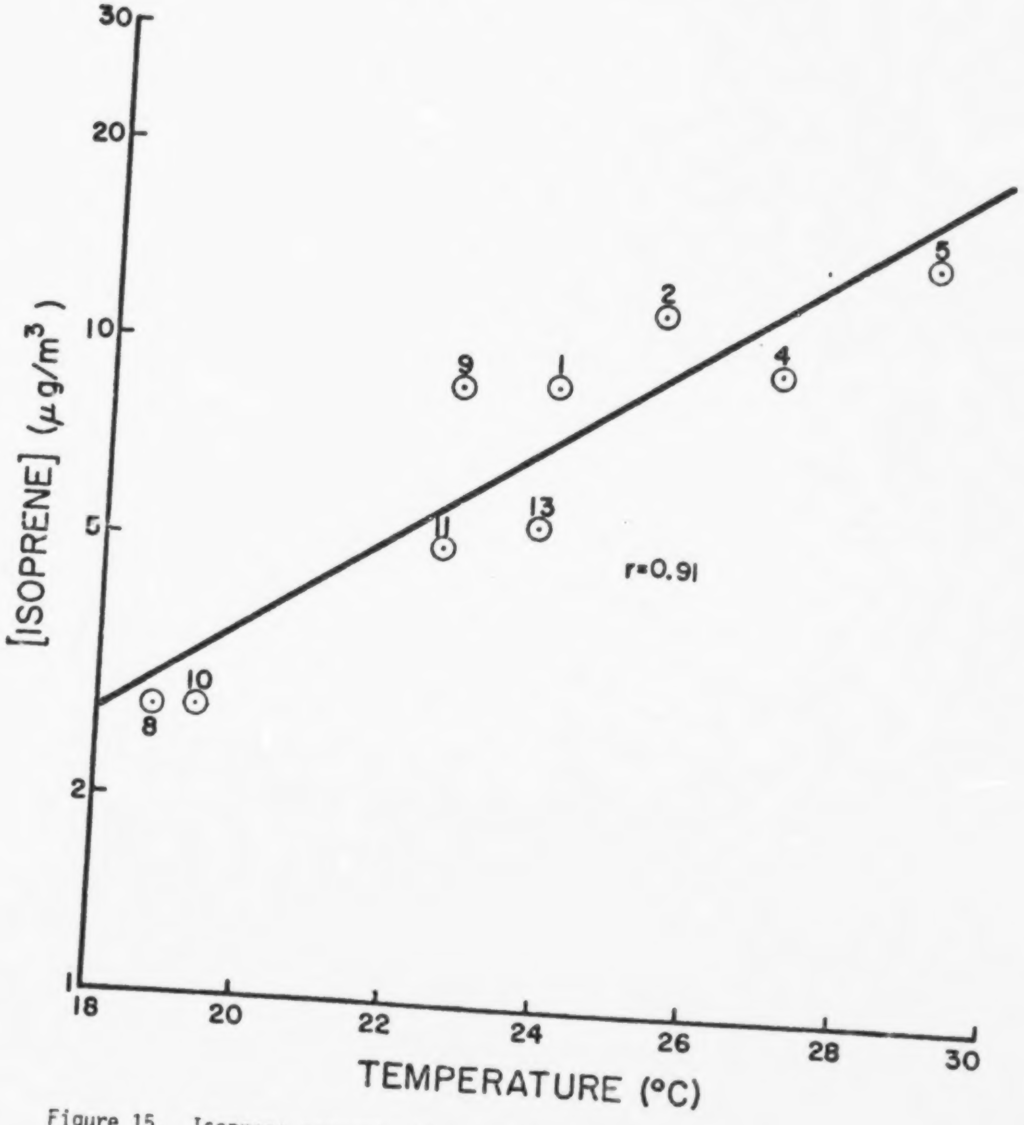

Figure 15. Isoprene concentration 6 m above the canopy as a function of temperature.

flux data exhibit an exponential relationship between isoprene flux and ambient temperature shown as line 1 in Figure 16; the correlation coefficient for the best-fit line was 0.65. The flux of isoprene predicted by this functional relationship at an ambient temperature of 30°C equaled 8,010 $\mu g/m^2$-hr.

Ambient levels of isoprene over the forest canopy can be predicted using a simple Gaussian dispersion model. Model inputs corresponded to meteorological conditions present when a flux of 1,610 $\mu g/m^2$-hr was determined for the forest. Isoprene concentrations measured at 6 levels above the canopy averaged 7.6 $\mu g/m^3$. Predicted concentrations for the 6 levels averaged 7.0 $\mu g/m^3$. This simple calculation suggests that the calculated fluxes are reasonably compatible with the ambient concentrations measured above the canopy.

It is interesting to note that Peterson and Tingey, utilizing a simple dispersion model which included a reactive sink term, calculated maximum summertime isoprene levels for a simulated southeastern United States environment of approximately 20 $\mu g/m^3$ (19). The isoprene flux utilized in the modeling effort by Petersen and Tingey was assumed to equal 16,500 $\mu g/m^2$-hr for a leaf temperature of 30°C. Isoprene fluxes predicted in previous studies from the bag enclosure technique for a bag temperature equal to 30°C and a biomass equal to that estimated for the forest site ranged from 7,200 to 9,400 $\mu g/m^2$-hr (42,49). These values lie within 20% of the isoprene flux predicted with the tower data at 30°C.

Fifteen branch enclosure samples were collected at the test site in Pennsylvania from the five dominant hardwood species which were known isoprene emitters. The isoprene emission rates calculated with these data (Figure 12) were then used with a biomass factor of 379 g/m^2 (Table 7) to estimate the isoprene flux from the forest. Data for the enclosure samples are summarized

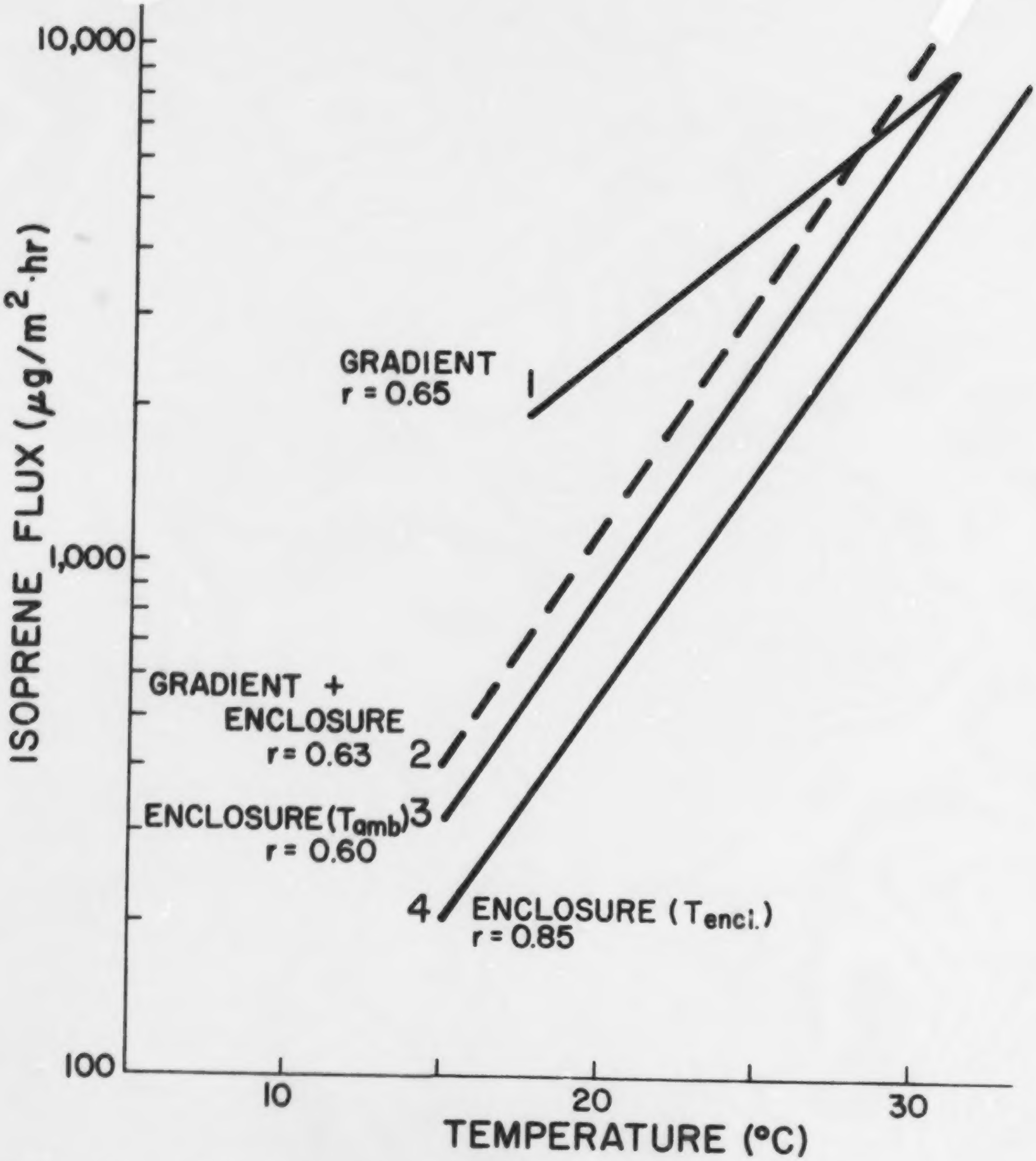

Figure 16. Isoprene flux versus ambient temperature measured at 6 m above the canopy from the gradient profile data (line 1), the gradient profile and enclosure data (line 2), and only the enclosure data (line 3). Line 4 is from the enclosure data versus enclosure temperature.

in Table 17. Ambient temperatures occurring during the sampling periods ranged from 11°C to 27°C and atmospheric conditions were slightly unstable to unstable. The estimated emission fluxes ranged from 106 to 18,100 $\mu g/m^2$-hr with mean and median values equal to 3,010 and 1,180 $\mu g/m^2$-hr.

As indicated previously, the isoprene emission fluxes determined with the enclosure data increased exponentially with the enclosure temperature. This strong correlation ($r = 0.85$) is shown as line 4 in Figure 16. The enclosure data show a similar exponential relationship with ambient temperature measured above the forest canopy. This relationship, shown as line 3 in Figure 16, has essentially the same slope as line 4, but line 3 has a lower correlation coefficient ($r = 0.60$). The difference between line 3 and line 4 is thus the result of an effective difference of approximately 2.5°C between the enclosure temperature and ambient temperature. This difference in temperature possibly reflects heat build-up in the enclosure during the sample period; elevated enclosure temperatures were particularly evident if the sample was collected in direct sunlight and condensation on the inner enclosure wall occurred. The temperature difference may also represent the difference between vegetation or leaf temperature and air temperatures. During the sampling procedure, the enclosure temperature probe is secured along the branch and shaded from sunlight. As a result, the recorded enclosure temperature probably corresponds to a composite vegetation-air temperature. A third reason for the differences between ambient and enclosure temperatures is that air temperatures near the ground within the canopy are typically warmer than those measured in the free stream above the canopy. Daytime temperatures near the surface will almost always be higher than temperatures measured above the canopy.

In order to compare directly the fluxes determined via the gradient profile

TABLE 17. ISOPRENE EMISSION FLUXES AND AMBIENT METEOROLOGICAL CONDITIONS FOR ENCLOSURE SAMPLES, PENNSYLVANIA

Specie	Date	Time (EST)	Isoprene Flux ($\mu g/m^2$-hr)	Heat Flux* (W/m^2)	Monin-Obukhov* Length (m)	T^a (°C)	T^{b}* (°C)	u_z*	σ_θ*	Radiation (Ly/min)	RH* (%)
White Oak	7/30	1210	3,070	....	....	25.5	....	....	....	....	....
	8/8	1338	379	65	- 52	28.3	27.2	2.2	30	.96	59
Black Oak	8/3	1446	941	....	....	23.3	....	....	....	....	....
	8/20	1237	18,100	38	- 30	34.4	23.2	1.4	27	1.24	54
Chestnut Oak	8/7	1217	1,180	73	- 70	23.3	23.4	2.1	30	....	62
	8/14	1200	1,710	182	-228	26.1	22.8	4.4	26	1.17	60
	8/14	1229	2,080	146	-154	23.9	22.6	3.5	33	.52	61
	8/14	1303	280	86	-158	21.7	21.8	3.0	23	.12	65
	8/16	0600	106	79	- 63	11.1	11.2	2.2	23	.03	76
	8/16	1002	483	164	-115	16.7	15.6	3.8	25	1.15	60
	8/16	1353	497	180	-104	20.0	18.4	3.7	26	1.23	49
	8/16	1745	315	66	- 23	17.2	18.8	1.3	28	.27	45
Black Locust	8/9	1114	2,870	59	- 56	27.8	24.0	2.0	30	1.31	49
	8/20	1306	5,460	36	- 27	28.9	23.3	1.4	31	1.24	53
Scarlet Oak	8/8	1044	7,660	93	- 94	28.9	24.9	3.0	24	.61	78

* Meteorological parameters determined from data collected on the gradient profile tower during the enclosure sample period.

[a] Bag enclosure temperature

[b] Ambient temperature

and enclosure techniques, it is necessary either to decrease the observed enclosure temperature by approximately 2.5°C to account for the differences described above or to use the line 3 results where emission fluxes from the enclosure data are related to the existing ambient temperature. Since both lines 3 and 4 have the same slope, in practice either approach will yield similar results in comparison to the gradient profile data (line 1).

Such a comparison based upon line 3 shows relatively good agreement between the fluxes predicted with enclosure and gradient profile data. At 30°C ambient, the fluxes obtained from the enclosure and profile methods are approximately 7,300 and 8,000 $\mu g/m^2$-hr. At 20°C ambient, the respective fluxes are approximately 890 and 2,500 $\mu g/m^2$-hr. In view of the lack of gradient profile data at low temperatures, the large difference in fluxes at 20°C compared to the small difference at 30°C is not surprising. Consideration of the enclosure and gradient profile data together yields an exponential relationship with a correlation coefficient ($r = 0.63$) essentially identical to the coefficients from the separate data sets. Such a result suggests that the enclosure and profile data could be considered as a single data population.

A systematic error analysis of both techniques is presented in Appendix 2. This kind of analysis does not address questions concerning the effects of enclosing vegetation or the effects of non-ideal surface layer flow. However, an error analysis does provide insight into the expected accuracy and reproducibility of the actual measurements. For the Pennsylvania forest, the estimated overall error in a typical gradient profile experiment was ± 35%. Uncertainty in the zero plane displacement height and the isoprene concentration gradient caused essentially all of the estimated error. The error analysis also showed that the gradient profile method should be reproducible to within approximately ± 15% since the displacement height is relatively constant from one test to the next at a specific site.

The results of the error analysis for a typical enclosure sample yielded an overall error of ± 40%. The most significant sources of error were the biomass factor and the isoprene concentration in the emission sample. The technique is estimated to be reproducible to within approximately ± 20% because the biomass factor is fixed at a specific site.

Isoprene fluxes determined with the two methods easily agree within the estimated error limits at 30°C. At 20°C the upper limit of the calculated flux from the enclosure data is 1,200 $\mu g/m^2$-hr and the lower limit of the flux from the gradient profile data is 1,500 $\mu g/m^2$-hr. These results, along with the comparisons of the means and medians and the correlation given by line 2 in Figure 16, suggest that the fluxes from the two independent methods are in reasonably good agreement given the degree of variability present in the experimental conditions.

Data obtained by both methods were also used to test for simple functional relationships between isoprene flux and heat flux, Monin-Obukhov length (atmospheric stability), solar insolation, relative humidity, and the intensity of turbulence as measured by both $\sigma_\theta u_z$ and $T_z u_z$, where σ_θ is the standard deviation of the horizontal wind direction. Data from neither the gradiant profile method nor the enclosure technique exhibited an exponential relationship between isoprene flux and relative humidity, Monin-Obukhov length, or insolation. Isoprene fluxes calculated from the gradient profile data increased exponentially with heat flux ($r = 0.63$), but this kind of relationship did not exist for the enclosure data. In the case of the intensity of turbulence, the fluxes determined via the tower measurements increased exponentially with $\sigma_\theta u_z$ (r = 0.77) as seen in Figure 17. This relationship was not observed with fluxes estimated from the enclosure data. The flux of isoprene as measured by the gradient profile method also showed a strong correlation (r = .90) with the product of ambient temperature and wind speed, $T_z u_z$ (Figure 18), while the enclosure method did not exhibit this strong correlation. These differences suggest that the flux of isoprene is dependent upon the ventilation rate in the forest and that either the enclosure technique does not adequately simulate this ventilation pattern or that the ventilation effect is only important near the top of the canopy where the bulk of the biomass is located.

Washington forest site. Thirteen vertical profile measurements of the alpha-pinene flux were performed in the Washington forest during the period September 18 to November 29, 1980. Four tests had to be discarded because a shift in wind direction resulted in insufficient fetch; one test was not considered because an alpha-pinene concentration gradient could not be ascertained. Ambient alpha-pinene concentrations below the detection limit of 0.02 $\mu g/m^3$ were encountered in one test and therefore a flux could not be calculated. All tests were conducted in slightly stable to slightly unstable meteorological conditions as indicated by the ambient temperature gradient. Insolation for the tests ranged from near zero to 0.74 Langleys/min. Ambient temperature ranged from 9°C to 24°C. Wind speed at the mid-point of the sample array (34.6 m) varied from 1 to greater than 4 m/s. Five tests were conducted in conditions considered typical for the area: cool, rather high humidity, and wind speed less than 2 m/s. In two cases, however, moderate temperatures, low humidity, and moderate wind speeds prevailed. In general, these two groups behaved quite differently and this will be pointed out in the

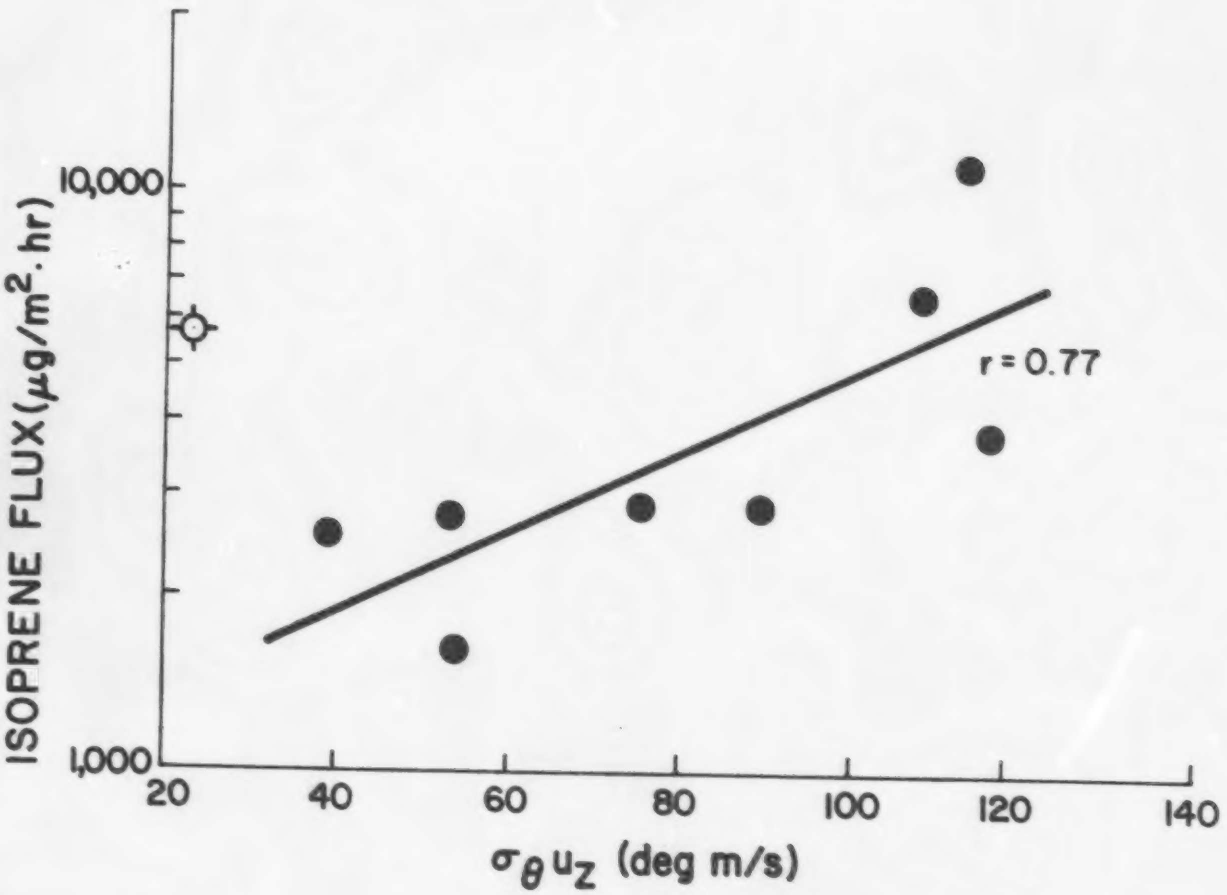

Figure 17. Isoprene flux from the gradient profile method versus turbulent intensity.

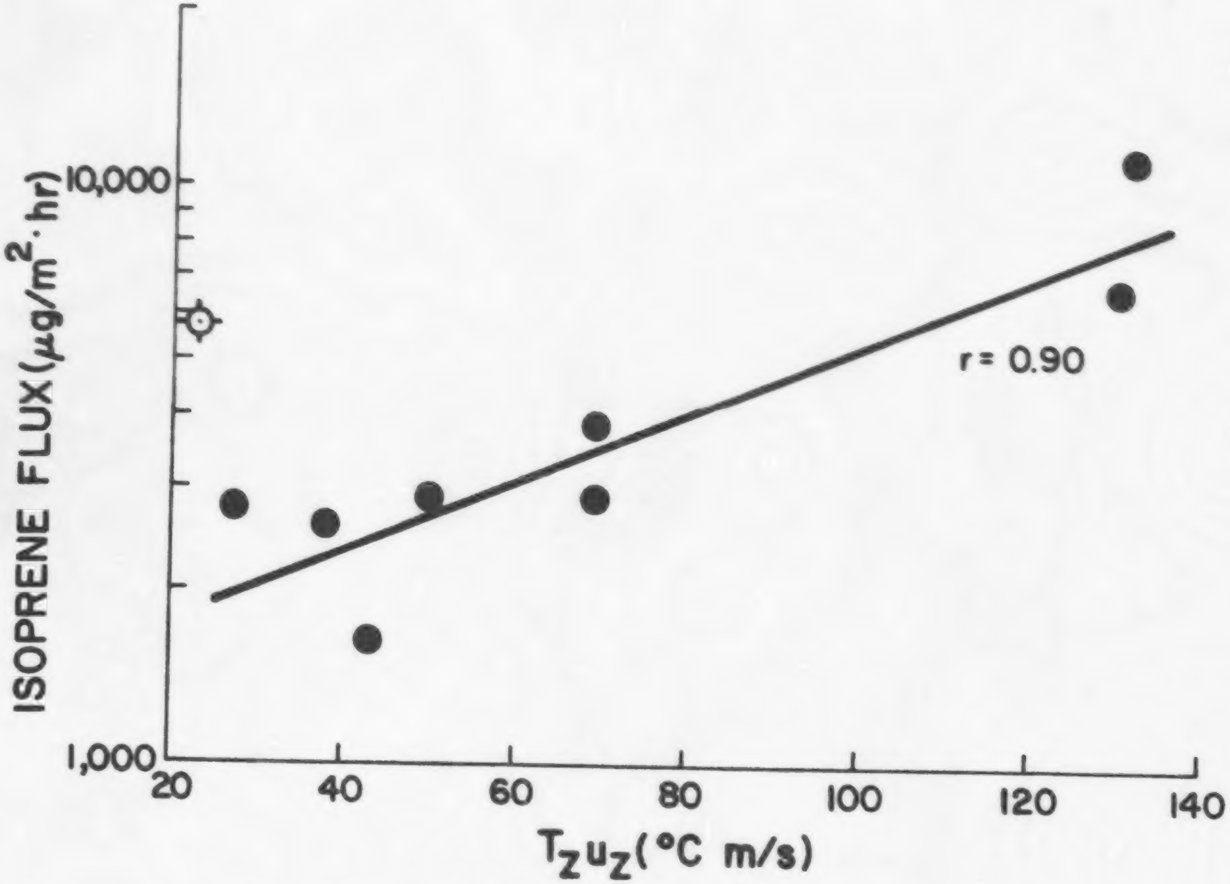

Figure 18. Isoprene flux from the gradient profile data versus $T_z u_z$ measured at 6 m above the canopy.

discussion. Typical profiles of temperature, wind speed, and alpha-pinene are shown in Figure 19 and the data for all profiles are summarized in Table 18. The average alpha-pinene flux for the seven tests was 443 $\mu g/m^2$-hr with a range from 71 to 1,320 $\mu g/m^2$-hr; the median flux was 230 $\mu g/m^2$-hr.

Concentrations of alpha-pinene collected at the sample height mid-point 4 m above the canopy exhibited a strong exponential relationship with relative humidity (Figure 20). If the two tests conducted under atypical meteorological conditions are not included, a near perfect correlation is obtained (r = .99). The calculated flux of alpha- pinene also exhibits this same strong dependency as shown in Figure 21 (r = .99). The correlation of alpha-pinene flux with ambient temperature was weak (r = -0.45). Therefore, it appears that relative humidity is the dominant environmental parameter which controls the emissions of alpha-pinene from Douglas Fir. This was observed only when tests were conducted in relatively high humidity conditions (>60%). Tests 2 and 11 were performed under a combination of low humidity and high wind speed conditions and did not exhibit this same relationship as can be seen in Figure 21. During both of these tests, heat fluxes were relatively high, the level of turbulence (σ_θ u_z) was relatively high, and the relative humidity was low. If the calculated alpha-pinene flux is examined versus the ratio of relative humidity to wind speed for all seven tests (Figure 22), a relatively good correlation is obtained (r = .71). A more thorough examination of the role this ratio may play in determining alpha-pinene emission rates is required before the exact nature of this relationship can be fully understood. The observed fluxes showed no significant correlation with heat flux, Monin-Obukhov length, time of day, intensity of turbulence, or ambient temperature.

A simple Gaussian volume source model was utilized to predict the ambient

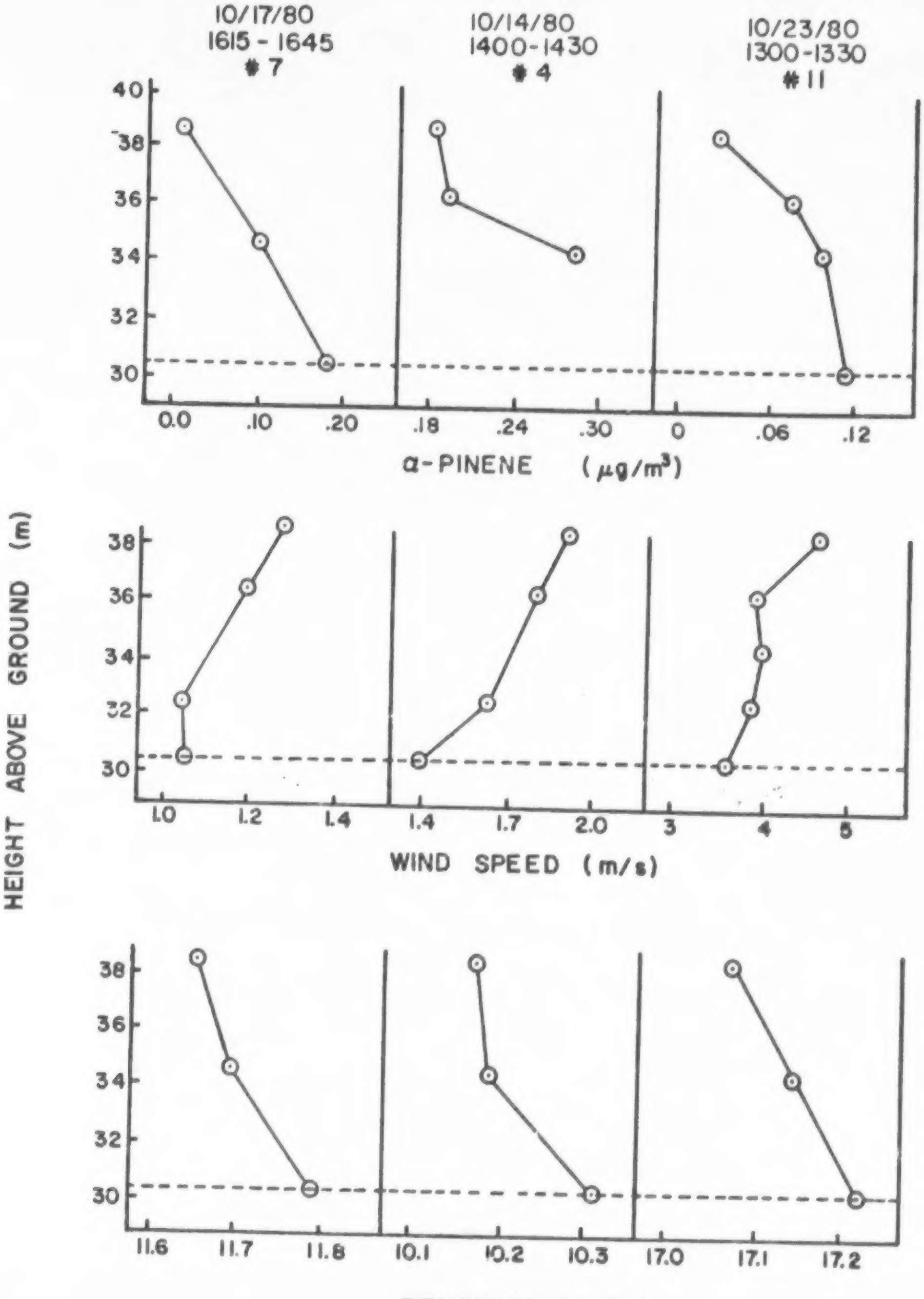

Figure 19. Typical profiles of wind speed, temperature and alpha-pinene concentration above the coniferous forest.

TABLE 18. ALPHA-PINENE EMISSION FLUXES AND METEOROLOGICAL PARAMETERS FROM GRADIENT PROFILE EXPERIMENTS, WASHINGTON.

Test No.	Date (1980)	Time (PST)	Alpha-pinene Flux* ($\mu g/m^2$-hr)	T_z* (°C)	u_z* (m/s)	σ_θ* (34 m) (deg)	Radiation (Ly/min)	Relative Humidity (%)	Heat Flux* (W/m^2)	Monin-Obukhov Length* (m)	e_u (%)	ΔT_o (°C)	ΔT_p (°C)
1	9/18	1345	1320	13.5	0.9	-	0.1	88	7	-325	3	-.08	-.02
2	9/25	1630	76	23.6	2.7	19	0.2	34	28	-111	3	.39	-.05
4	10/14	1300	289	10.2	1.7	8	0.3	77	13	-773	7	-.01	-.02
5	10/15	1345	91	11.3	1.7	7	0.5	62	22	-467	11	-.21	-.03
7	10/17	1515	148	11.7	1.2	11	0.2	66	7	-469	8	-.04	-.02
11	10/23	1200	230	17.1	4.0	27	0.7	32	60	-2160	8	-.08	-.05
15	11/20	1430	946	9.7	1.3	7	0.1	86	-8	468	3	-.03	+.02

* All values determined for mid-point of the sampler array (34.6 m, 4 m above the canopy). Relative humidity is from a dew point sensor located at 30.5 m and radiation is from a sensor at 39.6 m.

$e_u \equiv$ mean percent error between observed and predicted (best-fit) wind speeds (at 30.5, 32.6, 34.6, 36.3, and 38.7 m)

$\Delta T_o \equiv$ observed temperature gradient between 32.6 m and 38.5 m.

$\Delta T_p \equiv$ predicted (best-fit) temperature gradient between 32.6 and 38.5 m.

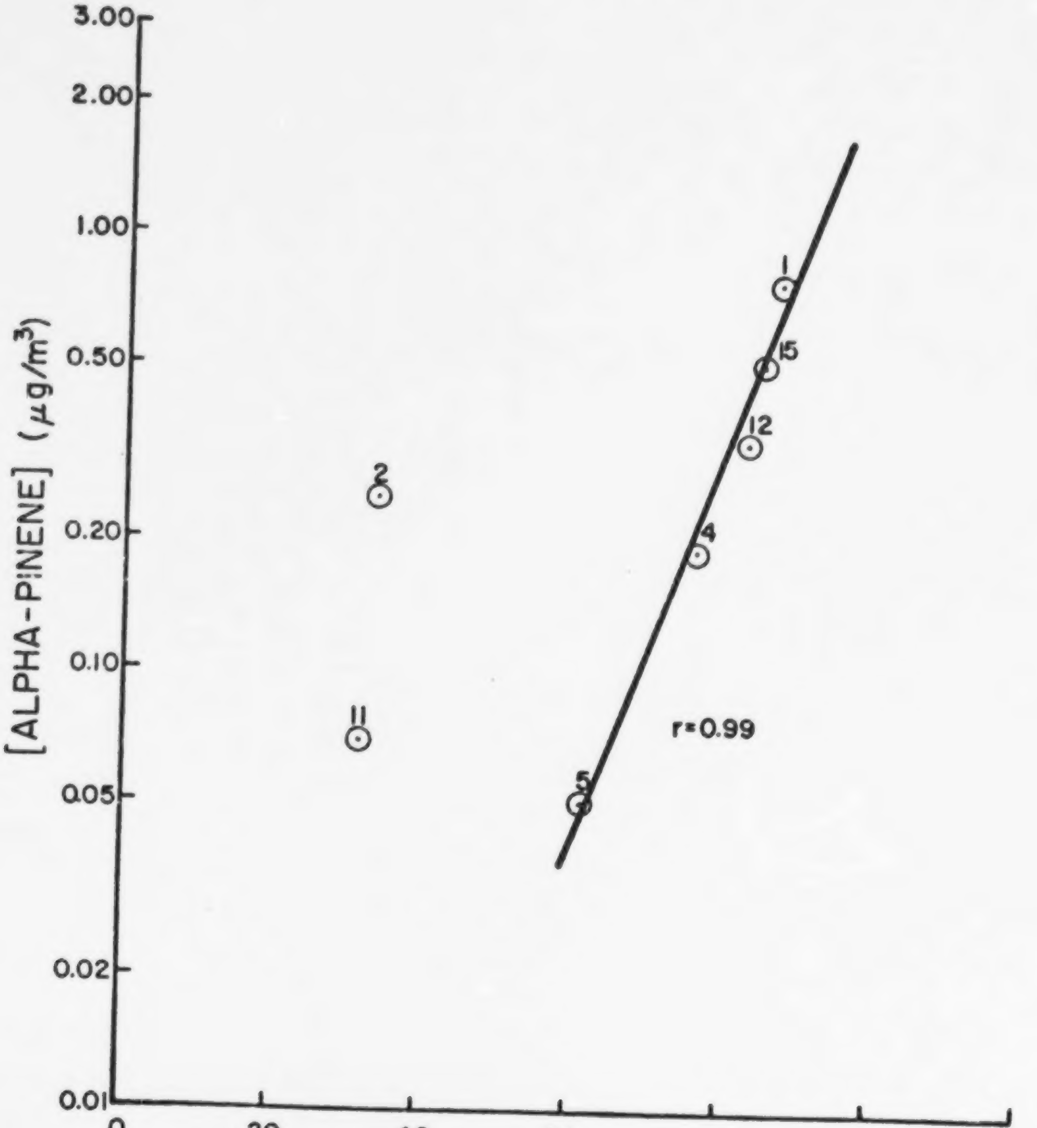

Figure 20. Alpha-pinene concentration at 34.6 m as a function of relative humidity.

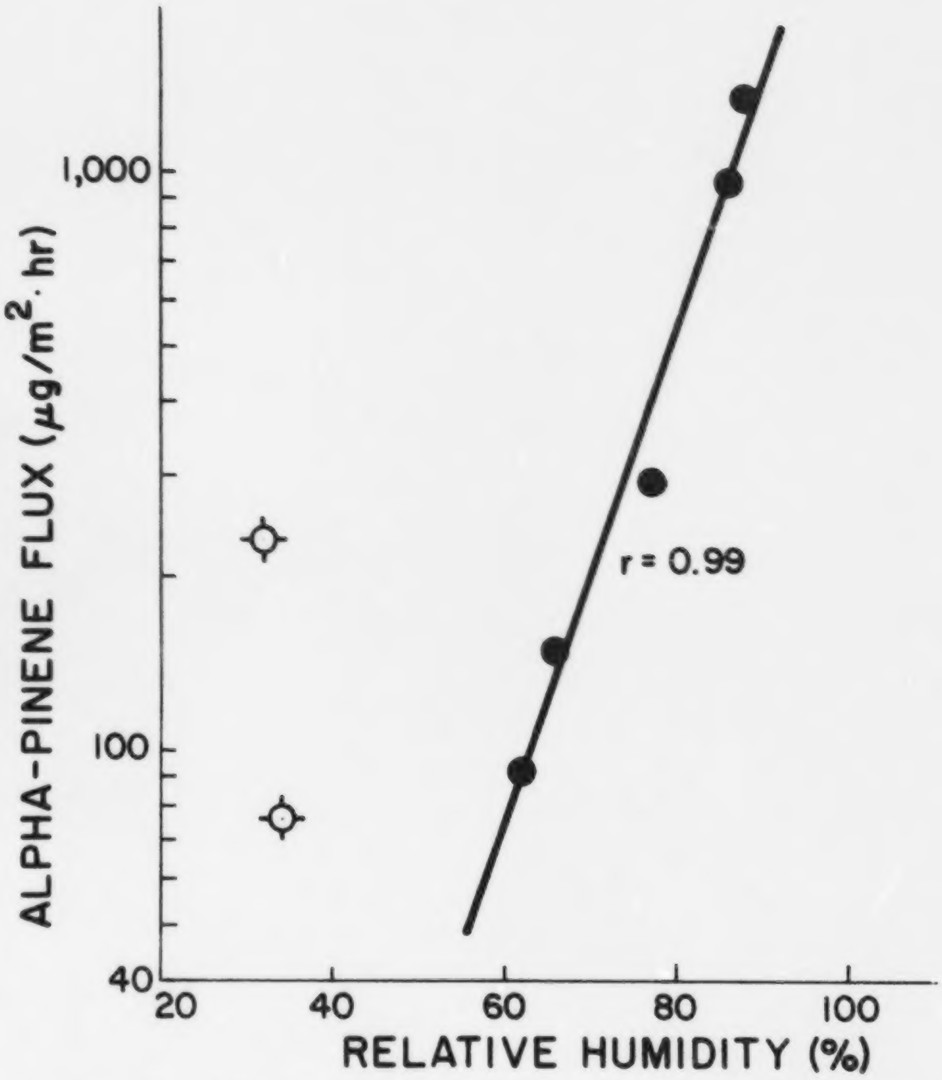

Figure 21. Alpha-pinene flux from the gradient profile data versus relative humidity, Washington.

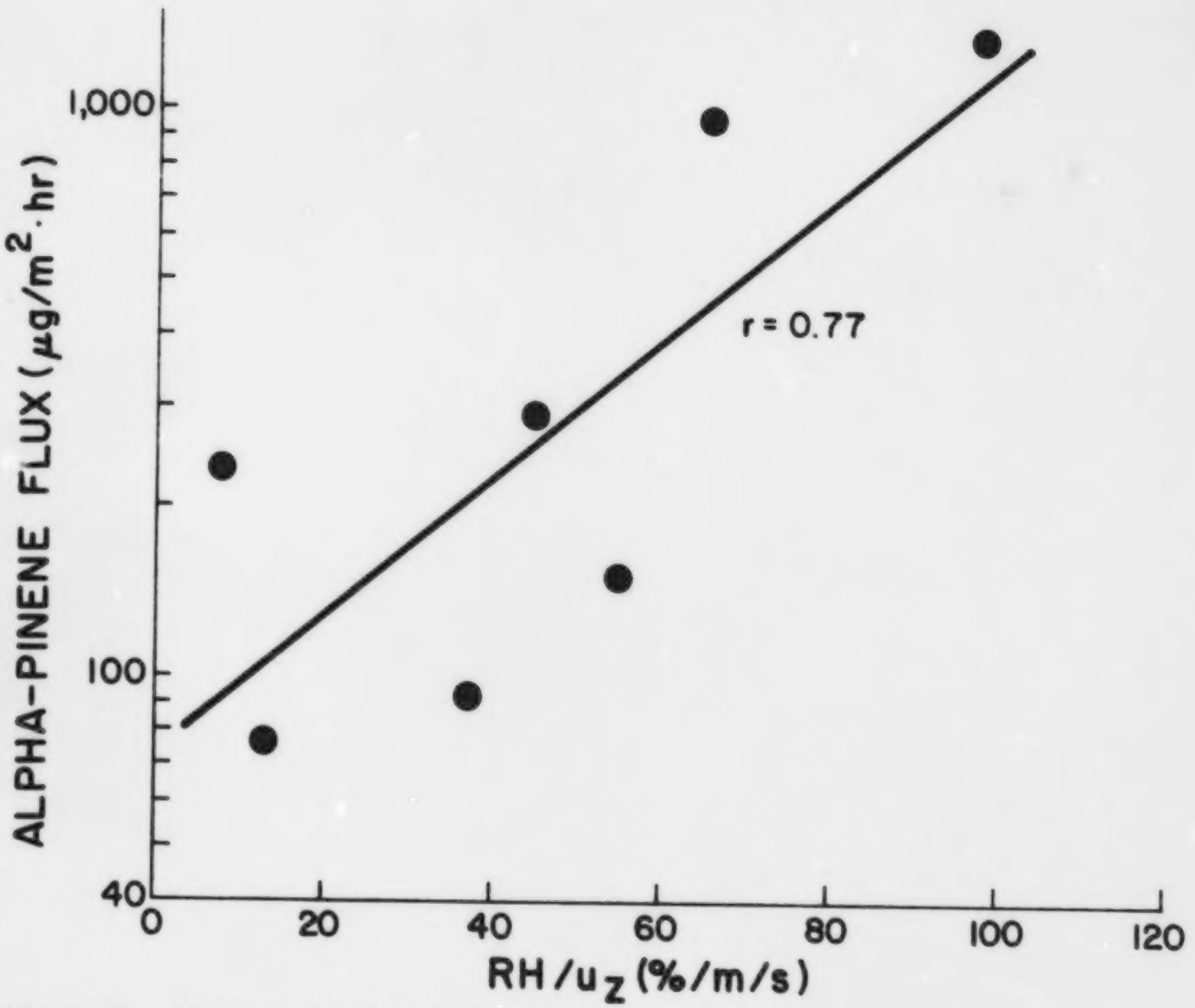

Figure 22. Alpha-pinene flux from the gradient profile data versus the ratio of relative humidity to wind speed, Washington.

concentrations above the canopy for representative meteorological and emission conditions. The model approximates an area source with a large number of line sources. A uniform upwind fetch of 1600 m was assumed with 1600 line sources equally spaced through the area. The height of the source was taken to be equal to the approximate height of maximum foliar density, 21 m. An initial vertical plume dimension, σz_0, was chosen to provide for initial dispersion throughout the canopy. The beginning concentration would then be maximum at 21 m, diminishing to $0.1C_{max}$ at the canopy top and at the approximate bottom edge of foliage. Although the stability was approximately neutral, Pasquill stability class 3 was chosen to account for the roughness of the canopy. Two base cases were considered: (1) an alpha-pinene flux of 946 $\mu g/m^2$-hr with a wind speed of 1.3 m/s (Test 15), and (2) an alpha-pinene flux of 76 $\mu g/m^2$-hr with a wind speed of 2.7 m/s (Test 2). Results are summarized in Table 19. Predicted alpha-pinene concentrations at the canopy top were a factor of 2 higher than observed in the first case and approximately a factor of 2 smaller in the second case. Above the canopy, the model overestimated the observed concentration in the high flux case and underestimated the observed level in the low flux case. These differences could be due to an insufficient treatment by the model of the wind speed gradient which existed above the canopy. The wind speed measured at 4.1 m above the canopy was used for the wind speed input. The model results shown in Table 19 indicate that concentrations of alpha-pinene less than 4 $\mu g/m^3$ could be expected for fluxes as high as 900 $\mu g/m^2$-hr.

Seventeen branch enclosure samples were collected during the period September 25 to November 20, 1980. Three were not considered because of analysis problems while one was collected improperly and had to be discarded. The following discussion concerns the remaining 13 samples. As will be shown

TABLE 19. COMPARISON BETWEEN MEASURED AND PREDICTED α-PINENE CONCENTRATIONS FOR (a) FLUX = 946 $\mu g/m^2$-hr AND u_z = 1.3 m/s (Test 15) AND (b) FLUX = 76 $\mu g/m^2$-hr AND u_z = 2.7 m/s (Test 2)

Height Above Canopy (m)	Measured Concentrations ($\mu g/m^3$)	Predicted Concentrations ($\mu g/m^3$)
(a)		
0	1.77	4.0
8.2	.54	3.2
(b)		
0	.44	0.20
8.2	.38	0.09

below, it is convenient to group the samples into two groups: those with branches which were distinctly wet during sampling and those with branches which were dry to the touch when sampled.

Eleven samples from the dominant species Pseudotsuga (Douglas Fir) were collected while one each was obtained from Thuja plicata (Western Red Cedar) and Tsuga heterophylla (Western Hemlock). Four were collected when branches were very wet, either from rainfall or dew, and the remaining nine were dry samples. The average flux calculated from these 13 samples was 146 $\mu g/m^2$-hr with a range from 9 to 700 $\mu g/m^2$-hr. The median flux obtained with the enclosure method was 46 $\mu g/m^2$-hr. The enclosure sample data are summarized in Table 20. Samples 15 and 16 were collected 15 minutes apart from a different tree and exhibited a similar degree of precision; calculated fluxes were 86 and 74 $\mu g/m^2$-hr. This indicates that the enclosure method is very reproducible under constant environmental conditions. An error analysis described in Appendix 2 estimated that samples collected under constant physiological conditions should agree to within less than 20%. Any differences greater than ±20% observed between samples, therefore, should be an indication of the effects of changing environmental conditions upon the emission rate, and not random errors associated with the measurement technique. For example, although samples 8 and 9 were branches from the same tree, they were collected two days apart under differing environmental conditions and exhibited differing fluxes of 245 and 700 $\mu g/m^2$-hr, respectively.

The enclosure data show no significant relationship with relative humidity as illustrated in Figure 23. Sample 11 is not considered representative of ambient conditions as direct sunlight on the bag caused an increase in bag temperature markedly above ambient temperature. When examined in relation to

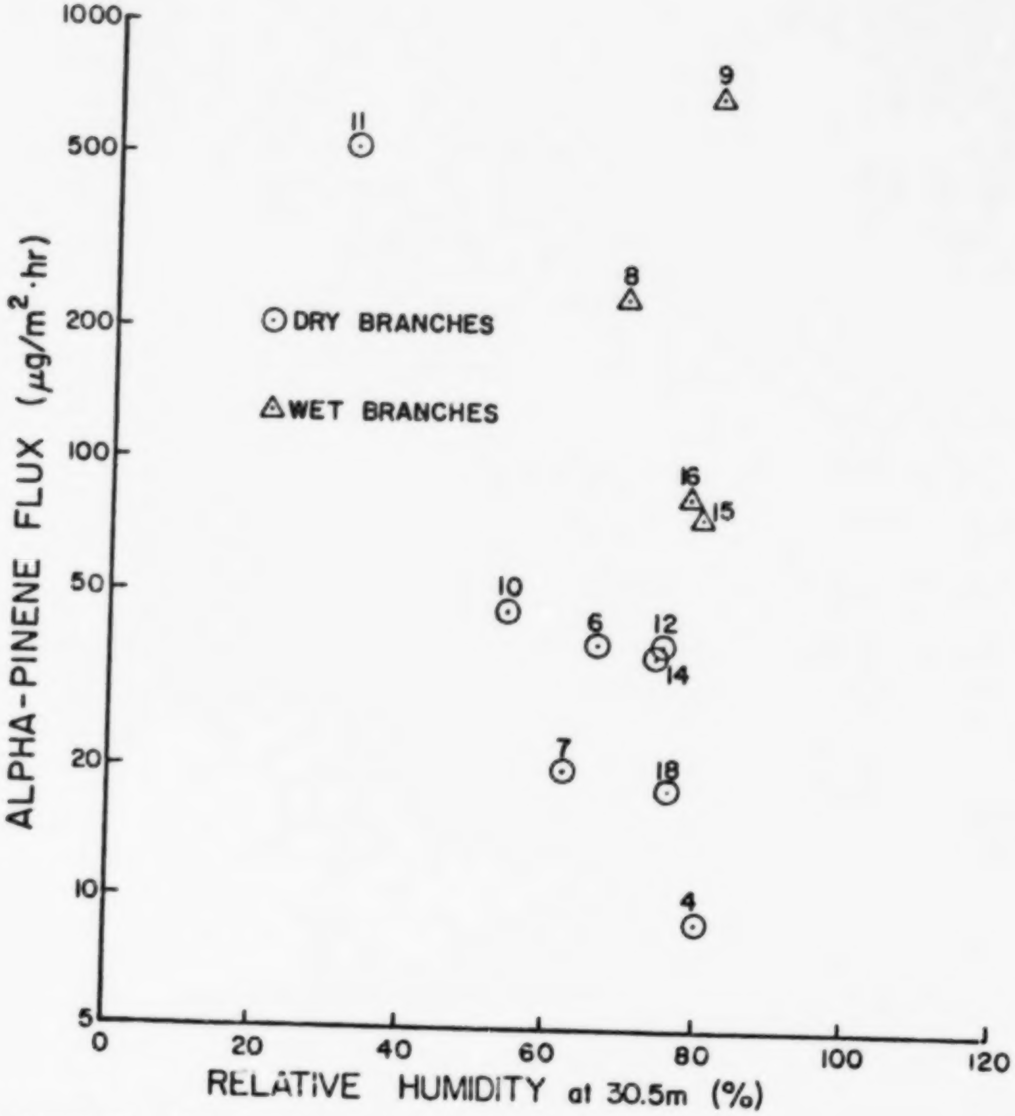

Figure 23. Alpha-pinene flux measured by the enclosure method as a function of the ambient relative humidity.

TABLE 20. ALPHA-PINENE EMISSION FLUXES AND AMBIENT METEOROLOGICAL PARAMETERS FOR ENCLOSURE SAMPLES, WASHINGTON

Sample #	Specie	Date	Time (PST)	Alpha-pinene Flux ($\mu g/m^2$-hr)	Heat Flux* (W/m^2)	Monin-Obukhov Length* (m)	T^a (°C)	T^{b}* (°C)	u_z* (m/s)	σ_θ* (deg)	Radiation (ℓy/min)	Relative Humidity (%)
1	Doug Fir	9/25	1300	57	....	....	15	....	....	....	....	....
4	Doug Fir	10/13	1630	9	1	-2900	9	10.7	0.7	14	0.05	80
6	Doug Fir	10/15	1500	39	17	-1530	12	11.1	2.2	7	0.39	66
7	Cedar	10/16	1230	20	30	- 342	13	11.5	1.6	7	0.83	62
8	Doug Fir	10/18	0945	245	11	- 224	9	11.1	1.0	7	0.48	69
9	Doug Fir	10/20	1515	700	2	-1120	13	13.3	1.0	11	0.20	81
10	Hemlock	10/22	1230	46	12	- 924	10	13.0	1.7	6	0.68	54
11	Doug Fir	10/23	1015	528	7	-17000	22	15.2	4.1	15	0.62	32
12	Doug Fir	11/19	1445	39	- 1	920	12	12.4	0.9	7	0.34	75
14	Doug Fir	11/19	1500	37	- 2	137	10	12.2	0.7	10	0.24	74
15	Doug Fir	11/20	0930	76	- 5	69	8	8.9	0.9	9	0.10	80
16	Doug Fir	11/20	1000	84	- 4	475	10	9.1	1.0	9	0.16	78
18	Doug Fir	11/20	1130	18	- 6	127	9	10.1	0.9	15	0.04	76

a) Bag enclosure temperature

b) Ambient temperature

* Determined from the gradient profile tower during enclosure sample periods.

the ambient temperature measured at the mid-point of the sensor array above the canopy (34.6 m), the enclosure data exhibit an interesting relationship as seen in Figure 24. Two distinct groups of data are observed. The upper group are samples which were collected from branches dripping with moisture, unlike the bottom group which were dry when sampled. At any given temperature, the flux measured from a wet branch was approximately one order of magnitude larger than the flux observed from a dry branch.

It appears that if a basically dry branch is enclosed in a bag and dry air pumped in, the air in the bag will equilibrate at some low relative humidity. On the other hand, if a branch, dripping wet, is enclosed and dry air added, the humidity should equilibrate at some elevated value. If one assumes there is sufficient water on each of the wet branches to saturate the air in the bag and there is an insufficient amount present on the dry branches to significantly increase the humidity of the dry air, the dry and wet branches should fall into two relatively constant humidity groups. With humidity relatively constant in each group, it is then possible to examine the effect of temperature on the emission rates of alpha-pinene. Both groups of samples exhibit increasing emission rates with increasing ambient temperature (Figure 24).

Branch emission rates were also examined versus solar insolation, eddy heat flux, wind speed, percent relative humidity/wind speed, and time of day. No significant trends or correlations were observed.

An attempt was made to relate the fluxes observed by both methods to a common measured variable. However, unlike isoprene, the results precluded the use of this approach. No common functional relationship with either a single or multiple variable was observed in a comparison of the alpha-pinene fluxes

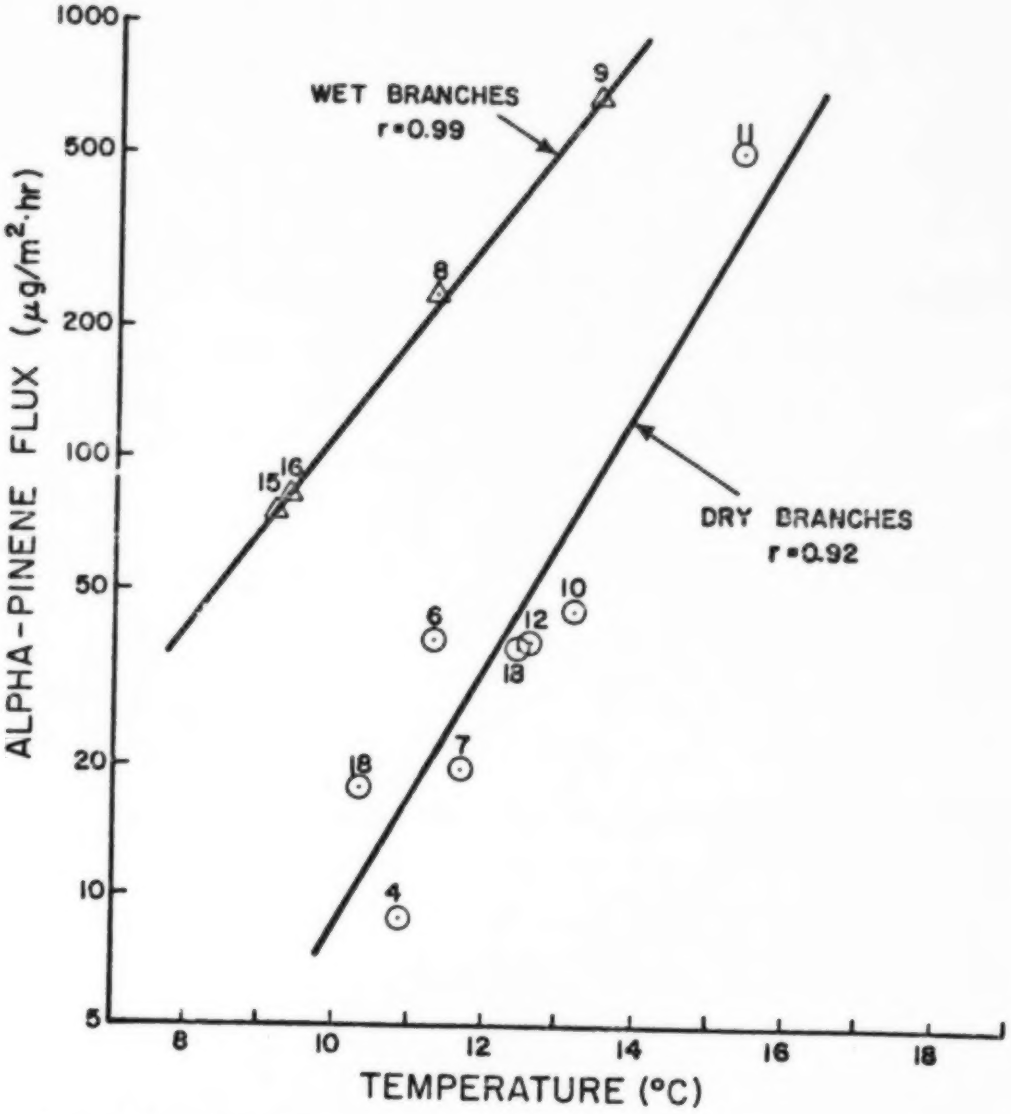

Figure 24. Alpha-pinene flux measured by the enclosure method as a function of ambient temperature.

obtained by the two methods. Certain qualitative observations can be made, however, which may offer insight into the results obtained by these two independent measurements of biogenic alpha-pinene emissions.

The mean fluxes calculated for the tower method and the enclosure procedure were 443 $\mu g/m^2$-hr and 146 $\mu g/m^2$-hr, respectively; the medians were 230 $\mu g/m^2$-hr and 46 $\mu g/m^2$-hr. The range of alpha-pinene fluxes measured with the gradient profile approach was 76 to 1320 $\mu g/m^2$-hr and the range measured with the enclosure procedure was 9 to 700 $\mu g/m^2$-hr. A sensitivity and uncertainty analysis of the two procedures was performed to determine the estimated errors in the tower and enclosure measurements. A complete description is provided in Appendix 2. Errors in the gradient profile measurements were estimated to cause less than approximately ±55% error in the calculated flux of alpha-pinene. The largest sources of error were the zero plane displacement height, the concentration gradient and the surface roughness length. With constant values of the displacement height and roughness length at a specific site, the method is estimated to be reproducible to within ±17%. Systematic errors in the enclosure measurements were estimated to cause a ± 40% error in the calculated flux. The mean alpha-pinene fluxes obtained with the two measurement techniques do agree within the estimated limits of uncertainty. but the median fluxes do not agree within the estimated error limits. However, in view of the observed importance of moisture and the number of dry branches sampled, this lack of agreement is not necessarily unexpected. The maximum flux measured with the enclosure method was approximately 50% of the maximum measured with the gradient profile method.

Both flux measurement techniques suggest alpha-pinene fluxes are dependent upon relative humidity as shown in Figures 21 and 24. The alpha-pinene flux determined with the gradient profile method increased with increasing humidity. The wet branches (high humidity) sampled with the enclosure method exhibited a higher flux than the dry branches (low humidity) at a given temperature. The enclosure data suggest that the alpha-pinene emission rate is not dependent upon the relative humidity measured at 34.6 m (Figure 23). Since the enclosure data suggest the emission rate is dependent upon the humidity inside the bag (high humidity vs. low humidity), it must be concluded that the humidity inside the bag is independent of the ambient humidity. This would mean any emission rates measured by the enclosure technique from vegetation whose emissions were humidity dependent would be representative only of the humidity inside the bag. These results are a strong recommendation for accurate measurement of humidity inside the bag in all future studies.

The enclosure data indicate that the emission rate is dependent upon the ambient temperature for both dry and wet branches. This strong relationship with temperature was not observed by the gradient profile technique. This could be due to a more dominant mechanism (humidity-dependent) masking the effects of a less important mechanism (temperature-dependent) in the ambient conditions under which the tower tests were conducted. More tests performed over a larger range of humidity and temperature need to be conducted before this can be concluded.

In summary, the comparisons between the two measurement techniques in Pennsylvania and in Washington have better defined the degree of reliability of emission flux estimates. Although the usefulness of data collected with the enclosure method have been disparaged previously, the results reported here as well as those previously described by Knoerr (15) show that the enclosure method yields emission fluxes quite similar to those obtained with totally independent techniques. The large errors prescribed to the enclosure procedures and necessary to resolve the difference between biogenic and anthropogenic hydrocarbon concentrations and emission levels simply do not exist in the data obtained in this study. It is true, however, that care is required to use the enclosure method, that enclosure conditions must be closely monitored in order to relate the data to ambient conditions, and that biomass factors must be developed from site specific inventories and representative biomass relationships.

With these requirements in mind, the enclosure technique is probably the preferred method for the development of regional biogenic emission inventories. The enclosure system is portable, easily operated by one person, and is not limited by idealized sites. In comparison, the gradient profile method involves considerable effort and instrumentation, the site requirements are restrictive to the point of being not practical, and the uncertainties in specifying the zero plane displacement height and property gradients reduce the applicability of the technique to the kind of comparative studies described in this report.

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APPENDIX 1

VEGETATION NEAR KONDOR'S SAW MILL
HELLAM TOWNSHIP, YORK COUNTY, PA.

A Report Submitted To
Air Pollution Research Section
Washington State University
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By

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Introduction - Studies of the hydrocarbon emissions of the natural vegetation are being conducted by the air pollution research group of Washington State University as part of a larger study of air pollution in the northeastern United States. A vegetational analysis of the forest adjacent to their sampling tower in York County, PA was conducted by me to provide background data. The character of the eastern deciduous forests has been reported in Braun (1935) and more recently for certain associations by Keever (1971). The forests of southeastern Pennsylvania have been characterized by Keever (1973). The woodland studied here is representative of second growth oak-chestnut formation.

The woodland sampled is at 40° 02' 30" N latitude, 76° 37' 30" W longitude in Hellam Township, York County, PA. It is on a level area 770' above sea level. About 0.7 mi N. there are steep ridges dropping to the Susquehanna River at 240'. Ridges of 1000' lie to the south. The area overlies Chickies sandstone formation. The woodland was selectively cut in the past as evidenced by numerous multiple trunked trees but it does not appear to have been cleared.

Methods and Materials

The overstory and understory were sampled simultaneously using the quarter method (Smith, 1966). Understory tree was taken as any tree 3 meters or taller but shaded by an overstory tree (Keever, 1973). Thirty sampling points were taken at 50' intervals along a line running WNW - ESE. Points near trails or borders were eliminated. The data were analyzed using a computer program developed by Prof. Kenneth Miller and the Computer Science Center of Millersville State College. The following parameters were analyzed for each species encountered:

$$\text{Relative density} = \frac{\text{number of individuals species X}}{\text{number of individuals of all species}} \times 100$$

$$\text{Relative dominance} = \frac{\text{total basal area of species X}}{\text{total basal area of all species}} \times 100$$

$$\text{Relative frequency} \quad \frac{\text{frequency of species X}}{\text{sum of frequencies for all species}} \times 100$$

See Smith (1966) for discussion. Relative density is essentially a percent of the total individual plants a given species contributes. Relative dominance represents a contribution to the community in terms of plant size. Relative frequency is a measure of the distribution of a given species through the community with higher numbers indicating a more uniform distribution. An importance number is a most useful comparative parameter obtained by adding the three figures obtained above.

Results and Discussion - Table I are the results of the data analysis. In the overstory four oaks *Quercus velutina*, *Q. prinus*, *Q. coccinea* and *Q. alba*, comprise 77.50% of the individuals present. They also comprise 71.02% of the relative dominance which indicates their size is in proportion to their numbers. *Liriodendron* is interesting in that it has a low (6.67) relative density but a much higher relative dominance in the overstory. This is because there are few individuals but they are large. This is characteristic of this successional species in old second growth forests.

When comparing understory to overstory one should note that the total basal area of the understory is only 14% of the combined total. Species present here are, therefore, relatively unimportant in terms of size even though they have large numbers of individuals present and thus exhibit a high relative frequency. In terms of relative frequency *Cornus florida*, *Nyssa sylvatica*, *Quercus prinus*, *Sassafras*, and *Acer rubrum* comprise 72.50% of the understory individuals. From the overstory only *Q. prinus* maintains a similar position. *Q. velutina* is markedly less which suggests a future decline in its importance in the overstory. *Sassafras*, *Q. prinus*, *Q. alba* and *Betula lenta* comprise 65.78% of the relative dominance. This indicates that the larger sized understory trees are in these species. In this context the overstory dominants *Q. prinus* and *Q. alba* maintain their understory position. *Q. coccinea* is absent in the understory. At present one can picture an understory with numerous small *Cornus* and *Nyssa* and fewer, larger *Sassafras*, *Q. prinus*, *Q. alba* and *Betula lenta*. If left undisturbed, in time, *Q. prinus* would become more important in the overstory, *Q. velutina* and *Q. coccinea* would decline and *Q. alba* would maintain its relative position. One would anticipate gains by *Nyssa sylvatica* and *Betula lenta*. *Acer rubrum* would maintain its relative position. *Cornus* will remain as an understory tree. Longer term predictions require data from the seeding and transfressive layer. Other species seen but not picked up in the samples include *Vibernum prunifolium*, *Carya tomentosa*, *Carya ovalis* and *Tsuga canadensis*.

Table II contains importance numbers for the dominant species in the overstory or understory and combined for both. If only one species was present, its importance number would be 300. Dividing importance numbers by three yields one a number comparable on a percentage basis. Quercus velutina, Q. prinus, Q. coccinea and Q. alba have a cumulative importance of 73.27 in the overstory. In the combined forest data their value is 45.70 which is lower than their true importance due to the large numbers of small trees in the understory. The understory is comprised of Nyssa, Sassafras, Betula lenta, Cornus, and Acer rubrum with a cumulative value there of 68.26. However, these sampe species contribute only 25.40 to the combined forest.

Summary - The forest sampled is representative of the oak-chestnut formation (Keever 1971,1973) of Pennsylvania. This stand is in a late successional stage as evidenced by the scattered Liriodendron, Robinia, Prunus serotina, and Betula lenta present in the overstory. Relative dominance values in the overstory probably best reflect the percentage contribution to the forest of leaf biomass and thus to hydrocarbon (or other) emissions to the atmosphere. The more comprehensive overstory importance numbers would provide an accurate (but more difficult to calculate) basis for such a comparison as well. If one compares these they are very similar. The data all point to the four oaks Quercus velutina, Q. prinus, Q. coccinea, and Q. alba as the dominant trees.

TABLE A1. Vegetation Survey at York County, PA Study Site

SPECIES	OVERSTORY[a]						UNDERSTORY[b]					
	No.	Basal Area	Rel Den	Rel Dom	Freq	Rel Freq	No.	Basal Area	Rel Den	Rel Dom	Freq	Rel Freq
Q VELUTINA	48	45.50	40.00	37.62	80.00	31.13	3	1.45	2.50	8.18	10.00	3.33
Q PRINUS	20	16.33	16.67	13.50	43.33	16.86	15	2.19	12.50	12.36	30.00	10.00
ROBINIA P	8	7.19	6.67	5.94	20.00	7.78	3	0.45	2.50	2.52	10.00	3.33
Q COCCINEA	12	12.89	10.00	10.66	26.67	10.38	0	0.00	0.00	0.00	0.00	0.00
Q ALBA	13	11.18	10.83	9.24	33.33	12.97	7	2.16	5.83	12.19	20.00	6.67
LIPIOD TUL	8	15.96	6.67	13.19	26.67	10.38	1	0.05	0.83	0.28	3.33	1.11
ACER RUBRUM	5	5.81	4.17	4.80	16.67	6.49	13	1.46	10.83	8.21	36.67	12.22
NYSSA SYL	1	0.32	0.83	0.27	3.33	1.30	17	0.91	14.17	5.10	40.00	13.33
BETULA LENTA	4	3.99	3.33	3.30	10.00	3.89	13	2.86	10.83	16.14	36.67	12.22
PRUNUS SER	1	1.79	0.83	1.48	3.33	1.30	1	0.59	0.83	3.35	3.33	1.11
SASSAFRAS	0	0.00	0.00	0.00	0.00	0.00	17	4.45	14.17	25.09	43.33	14.44
CORNUS FL	0	0.00	0.00	0.00	0.00	0.00	25	0.98	20.83	5.54	60.00	20.00
AMEL LAEVIS	0	0.00	0.00	0.00	0.00	0.00	2	0.10	1.67	0.54	6.67	2.22
CASTANEA DEN	0	0.00	0.00	0.00	0.00	0.00	3	0.09	2.50	0.49	10.00	3.33
TOTAL	120	120.96					120	17.74				

TABLE A1 continued.

SPECIES	COMBINED No.	Basal Area	Rel Den	Rel Dom	Freq	Rel Freq
Q VELUTINA	51	46.95	21.25	33.85	45.00	8.08
Q PRINUS	35	18.52	14.58	13.35	36.67	6.58
ROBINIA P	11	7.63	4.58	5.50	15.00	2.69
Q COCCINEA	12	12.89	5.00	9.29	13.33	2.39
Q ALBA	20	13.34	8.33	9.62	26.67	4.79
LIPIOD TUL	9	16.01	3.75	11.54	15.00	2.69
ACER RUBRUM	18	7.27	7.50	5.24	26.67	4.79
NYSSA SYL	18	1.23	7.50	0.88	21.67	3.89
BETULA LENTA	17	6.85	7.08	4.94	23.33	4.19
PRUNUS SER	2	2.38	0.83	1.72	3.33	0.60
SASSAFRAS	17	4.45	7.08	3.21	21.67	3.89
CORNUS FL	25	0.98	10.42	0.71	30.00	5.39
AMEL LAEVIS	2	0.10	0.83	0.07	3.33	0.60
CASTANEA DEN	3	0.09	1.25	0.06	5.00	0.90
TOTAL	240	138.70				

a) Total distance = 2492.99 ft; Number of stations = 30.
b) Total distance = 1640.20 ft; Number of stations = 30.

TABLE II

KONDOR WOODS

IMPORTANCE NUMBERS

Overstory			Combined	
Species	Imp. No.	Imp.No. 3	Imp. No.	Imp. No. 3
Q.velutina	108.75	36.25	63.18	21.06
Q.prinus	47.03	15.67	34.51	11.50
Q.coccinea	31.04	10.34	16.68	5.56
Q.alba	33.04	11.01	22.74	7.58
Liriodendron	30.24	10.00	17.98	5.99
Robinia	20.39	6.79	12.77	4.23

Understory			Combined	
Nyssa S.	32.60	10.86	12.27	4.09
Sassafras	53.70	17.90	14.18	4.72
Cornus f.	46.37	15.45	15.98	5.32
Betula l.	39.19	13.63	16.21	5.43
Acer r.	31.26	10.42	17.53	5.84

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APPENDIX 2

ANALYSIS OF ERRORS IN THE ENCLOSURE AND GRADIENT PROFILE METHODS

The accuracy of each measurement technique can be estimated using standard error analysis techniques (1). By definition, the uncertainty in a function dependent upon a number of variables is

$$\Delta F = \sum_{i=1}^{N} \frac{\partial F}{\partial X} \Delta X_i \qquad \text{(B-1)}$$

where N is the number of variables, $\partial F/\partial X_i$ is the derivative of the function with respect to each X_i and ΔX_i is the uncertainty in each variable.

In the case of the enclosure technique the emission flux depends in a linear manner upon seven variables as shown in Table B1. Each derivative in (B-1) can be determined directly from the equation for the flux in Table B1 and an analytical expression of (B-1) can be developed for the enclosure technique. To obtain a quantitative estimate of the error in the flux, the uncertainty in each X_i must be specified and data from a representative enclosure sample must be used in the analytical expression. The overall error as well as the contribution to the error of each variable can be calculated with this procedure.

In the analysis, it is assumed that errors in the measurement of the sample period and branch biomass are negligible. The volume of hydrocarbon free air was metered via a calibrated rotameter and the error in V_1 is estimated to be less than ± 5%. Dead volumes were estimated from measurements of the size of the branch, and errors as large as ± 50% are possible.

TABLE B1. ERROR ANALYSIS FOR A TYPICAL ENCLOSURE SAMPLE

	Variable	Value X_i	Estimated Uncertainty ΔX_i	Derivative $\partial F/\partial X_i$	Error $\mu g/m^2 \cdot hr$	(%)
S	Sample concentration	100 $\mu g/m^3$	± 10 $\mu g/m^3$	14.5 m/hr	145	10.8
B	Background concentration	50 $\mu g/m^3$	± 5 $\mu g/m^3$	2.08 m/hr	10	0.8
V_1	Sample volume	.060 m^3	±.003 m^3	20750 $\mu g/m^5 \cdot hr$	62	4.6
V_2	Dead volume	.010 m^3	±.005 m^3	10375 $\mu g/m^5 \cdot hr$	52	3.9
T	Sample time	0.20 hr	0	-	0	0
M	Branch biomass	20.0 g	0	-	0	0
F	Biomass factor	830 g/m^2	± 166 g/m^2	1.63 $\mu g/g.hr$	270	20
				TOTAL	539 $\mu g/m^2 \cdot hr$	± 40%

$$\text{Flux} = \frac{S(V_1 + V_2) - BV_2}{TM} \cdot F = 1349 \ \mu g/m^2 \cdot hr$$

As noted previously, the uncertainties in the measured hydrocarbon concentrations were approximately ± 10%. The forest biomass factor was obtained from site-specific forest inventories. For Pennsylvania, this inventory was used in a biomass relationship believed to be representative of the site. Biomass factors estimated from three other available biomass relationships varied by approximately ± 30% relative to the selected algorithm. In Washington, the biomass factor was obtained from previous forest surveys and biomass studies conducted at the site. For calculation purposes, the uncertainty in the biomass factor is estimated to be ± 20%.

These uncertainties in the various variables, data from a typical enclosure sample, and the contributions to the error associated with each variable are listed in Table B1. The total error calculated from this analysis is ± 40%. The results indicate that the sample concentration and biomass factor are the two most significant contributors to the overall estimated error. The calculations also show that the technique should be reproducible to within approximately ± 20% at a specific site since the biomass factor will be fixed in this case. Data obtained in Washington and described in a previous section indicate that this is a realistic estimate. Samples collected 15 minutes apart from different branches of the same tree agreed within 13%.

The error analysis for the gradient profile technique can be conducted in a similar manner. However, because the calculated flux is an extremely non-linear function of the independent variables, the derivatives can most easily be determined numerically for particular profile data sets.

The pertinent variables include the lower and upper wind speeds and temperatures, the zero plane displacement height, the surface roughness, and the hydrocarbon concentration gradient. As shown in Table B2, the uncertainty for each wind speed was taken to be ± 0.1 m/s, and the uncertainty in each temperature was assumed to equal ± 0.05°C. Since there is little guidance with respect to the value of the displacement height, the uncertainty was taken to be ± 0.1 h which roughly corresponds to the width of the range of suggested values. The uncertainty in the surface roughness was assumed to equal the standard deviation in the calculated value of z_0 for each forest site. For simplicity, the uncertainty in the concentration gradient was calculated as the overall error associated with a gradient calculated from two concentration measurement levels. For the prescribed ± 10% uncertainty in hydrocarbon concentrations, this yields an uncertainty of ± 14% in the concentration gradient.

The overall error estimated for the Pennsylvania profile data is ± 35% and the total error calculated from the Washington data is ± 55%. In each case, the uncertainties in the displacement height and the concentration gradient were the most significant sources of error. In Washington, the surface roughness also contributed significantly to the error. The calculations also show that the gradient profile technique should be reproducible to within approximately ± 14% in Pennsylvania and approximately ± 17% in Washington. These estimates of the reproducibility are based upon the assumption that the displacement height and surface roughness do not vary from test to test at a particular site.

Reference

1. P. R. Bevington, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York, NY, 1969.

TABLE B2. ERROR ANALYSES FOR THE GRADIENT PROFILE METHOD IN PENNSYLVANIA AND WASHINGTON

	Pennsylvania					Washington				
Variable	Value X_i	Uncertainty ΔX_i	Derivative $\partial F/\partial X_i$	Error $\mu g/m^2 \cdot hr$	%	Value X_i	Uncertainty ΔX_i	Derivative $\partial F/\partial X_i$	Error $\mu g/m^2 \cdot hr$	%
u_1	3.05 m/s	0.10 m/s	0	0	0	1.05 m/s	0.10 m/s	0	0	0
u_2	5.48 m/s	0.10 m/s	214	21	0.3	1.27 m/s	0.10 m/s	40	4.0	2.7
T_1	29.29°C	0.05°C	0	0	0	11.69°C	0.05°C	0	0	0
T_2	29.18°C	0.05°C	0	0	0	11.65°C	0.05°C	0	0	0
d	14.0 m	2.0 m	645	1290	20.0	21.4 m	3.1 m	14.6	44.5	30.0
z_o	0.94 m	0.16 m	438	70	1.1	3.54 m	1.65 m	7.3	12.0	8.1
dc/dz	0.366 $\mu g/m^4$	0.051 $\mu g/m^4$	18039	920	14.0	.019 $\mu g/m^4$	.003 $\mu g/m^4$	6907	20.7	14.0
		TOTAL		2301	±35%		TOTAL		81	±55%
F = 6600 $\mu g/m^2 \cdot hr$						F = 148 $\mu g/m^2 \cdot hr$				